**Nitrate sources, accumulation and reduction in groundwater from Northern Italy: Insights provided by a nitrate and boron isotopic database**

# Nitrate sources, accumulation and reduction in groundwater from Northern Italy: insights provided by a nitrate and boron isotopic database

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## Abstract

Large volumes of precious water resources are negatively affected by nitrate contamination, and the problem of the world population's exposure to this is becoming an even more pressing issue. To tackle this problem, the application of environmental isotopes has proven to be an effective method to identify the N origins and major transformations in different environments. In this work, nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and boron ($\delta^{11}B$) isotope analyses performed in the last twenty years in groundwater from shallow aquifers of the Po plain area, a complex hydrogeological system of European relevance, have been compiled in a comprehensive database together with major ionic contents; these data were integrated with additional original results, targeting areas not previously examined or complementing the available information. Such data, previously interpreted on the local scale, are examined at the Po plain scale, providing an understanding of the N sources and dynamics in the shallow aquifers, and defining the most important processes governing nitrate contamination in Northern Italy.

The most impacted groundwater is that hosted in the alluvial fans of the Alpine and Apennine foothills, due to a combination of high soil permeability and presence of intensive agricultural activities. Here, aquifers are characterized by fast circulation and by great water table depths. On the contrary, nitrate contamination is absent in most low plain areas, with shallow water table depths but lower soil permeability, due to the presence of denitrification processes. The $\delta^{15}N$ median values, calculated for each province, are significantly correlated with pig density. Hence, manure represents one of the main nitrate sources in groundwater from agriculture, the other being synthetic fertilizers. Isotopic compositions enriched due to denitrification are present in ~22% of the data, being responsible for nitrate abatement in groundwater affecting up to 70-80% of the original content.

The B systematics, in such a low geogenic-B context, proved the presence in the investigated area of another anthropogenic nitrate source of civil origin (i.e. sewage). While new results on the local B sources are reported, the garnering of all groundwater data allowed us to define the range of

the expected geogenic B signature ($\delta^{11}B$ =+13 ±2.5‰). This contribution is a significant step forward for the use of the coupled $\delta^{15}N$ - $\delta^{11}B$ toolbox in the study area, previously limited by a poor definition of the compositional end-members. This georeferenced set of hydrochemical and isotopic data will lay the foundations for future monitoring activities and advanced data treatment or modelling. In addition, since the hydrogeological setting of the investigated area shows common features to alluvial basins located near mountain ranges, the approach and the results presented in this study serve as a reference for other study areas worldwide.

**Key-words**

hydrogeochemistry, contamination, Po plain, pig manure, denitrification, sewage

## 1. Introduction

In the second half of the 20th century, following the so-called “green revolution”, agriculture in developed countries significantly increased crop production and livestock, with a concomitant enhanced use of synthetic and organic matter fertilizers (Tilman et al., 2001; Galloway et al., 2008). Although food availability increased, this produced diffuse pollution of nutrients in surface and groundwaters, currently representing a major environmental concern worldwide (Agren and Bosatta, 1988; Vitousek et al., 1997; Galloway et al., 2008). The resultant nitrogen accumulation on land and in waters frequently leads to the deterioration of freshwater and coastal ecosystem services, including water quality, fisheries, and amenity value.

In Europe, nitrate pollution by diffuse sources was first targeted by the Nitrate Directive (European Commission, 1991), followed by the Water Framework Directive (European Commission, 2000). The Nitrates Directive aimed to protect water quality across Europe by preventing nitrates from agricultural sources, also via the designation of "Nitrate Vulnerable Zones" (NVZs). These are territories that drain into polluted waters or waters at risk of pollution and contribute to nitrate pollution. As regards groundwater resources, polluted water, or those at risk of pollution, must be identified in groundwater containing, or that could contain (unless action is taken to reverse the trend), more than 50 mg/l of nitrates. Austria, Denmark, Finland, Germany, Ireland, Lithuania, Luxembourg, Malta, the Netherlands and Slovenia have decided to provide the same level of protection to their whole territory, rather than designate NVZs. In Italy, the Directives have led to the designation of large areas as being vulnerable to nitrate pollution, where the use of fertilizers, especially manure, was significantly restricted (170 and 340 kg N $ha^{-1}$ $yr^{-1}$ for NVZs and non-Nitrate Vulnerable Zones -nNVZs- respectively). Subsequently, and following the evidence collected that manure spreading might not be the only cause of nitrate contamination, the European Commission has granted Italy a derogation for the regions located in the Po plain (European Commission, 2011), allowing for an increase in manure spreading up to 250 kg N $ha^{-1}$ $yr^{-1}$ in NVZs, providing a higher Nitrogen Use Efficiency [NUE] of manure (*i.e.* the percentage of total nitrogen applied in the form of livestock manure that is available to crops in the year of application, considered to be 65% for slurry and 50% for farmyard manure).

One of the major difficulties with water contamination is the identification of the corresponding source(s) of pollution, a prerequisite for properly designing appropriate actions and remediation (Bronders et al., 2012). For this purpose, the application of environmental isotopes of dissolved nitrates (i.e.$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) has proven to be effective in a large number of cases (e.g. Aravena et al., 1993; Panno et al., 2001; Baily et al., 2011; Matiatos, 2016). More recently, the added value of analyzing the isotopic signature of boron ($\delta^{11}B$) in association with the specific isotope signature of nitrates has been demonstrated (Seiler, 2005; Widory et al., 2004; 2005; Saccon et al., 2013; Puig et al., 2017). Strontium and sulphate isotopes are randomly also used to reinforce this multi-isotopic toolbox (Vitòria et al., 2004; Nestler et al., 2011). In addition to the classical chemical approach, the coupled use of nitrate and boron isotopes - although not yet a routine technique - is gaining interest for policymakers and water quality administrators who are interested in identifying the nitrate sources. This approach is particularly important when the $NO_3$ concentrations are higher than the threshold value defined by the Water Frame Directive (WFD; 50 mg/l), which implies the definition of the poor chemical status of the quality of the water body. The need to discriminate between the different sources of pollution (i.e. sewage, animal manure, chemical fertilizer, natural soil mineralization) thus becomes crucial for any water exploitation and management (Komor, 1997; Widory, et al. 2004, 2005, 2013; Bronders et al., 2012).

The rationale for a coupled use of B and N isotopes is that these elements co-migrate in the groundwater, boron being unaffected by the redox reaction that causes nitrogen transformations (mainly denitrification/nitrification). However, boron is ubiquitous in water and its concentration strongly depends on the aquifer source rock and on the extent of the exchange of water with the fine aquifer matrix (Xiao et al., 2013). Many studies based on the coupled $\delta^{15}N$- $\delta^{11}B$ approach have aimed at defining a well-characterized frame of the geogenic $\delta^{11}B$ background (Palmer and Swihart, 1996 and reference therein), as well as of the anthropogenic components that could represent nitrogen and boron sources (see compilation in ISOBORDAT database; Pennisi et al., 2013).

Numerous studies have been conducted in Northern Italy in the last decade using a variety of hydrochemical and isotopic tools to tackle the sources, the processes and the factors controlling groundwater nitrate contamination. Previous studies on N compounds in groundwater from the Po valley, carried out in the period 1975-1995, considered $NH_4$, $NO_2$ and $NO_3$ molecules (e.g. Giuliano, 1995 and references therein). However, the N distribution in groundwater and its relation with other geochemical compounds often failed to unambiguously identify the nitrate source(s). Therefore, isotopic tools have started to be applied in the last twenty years, leading to a remarkable increase in produced data, nitrogen isotopes also often being associated to oxygen, hydrogen and boron isotopic systematics. As many studies were promoted by provincial or regional authorities, this copious amount of published data was generally interpreted on a local scale and, lacking a wider perspective, did not allow us to draw general conclusions at the Po basin scale, thus being of little interest for an international audience.

Although the watershed level is considered the most appropriate scale for the assessment of nutrient cycling and for the design of effective management and remedial plans (Baker and

Schussler, 2007; Billen et al., 2011), nitrate pollution studies are generally local and target only limited portions of large hydrogeological systems. Therefore, the literature lacks examples of regional studies covering areas such as the one investigated here, and based on a substantial amount of isotopic data.

The aim of this paper is to provide an understanding of N dynamics in the shallow aquifers of the Po plain area, representing a hydrogeological system of European relevance (WHYMAP, 2008), and with hydrogeological features common to alluvial basins located near mountain ranges worldwide. In industrialized countries, several sources may contribute to groundwater nitrate contamination, due to complex patterns of coexisting anthropogenic activities insisting on plains (intensive agriculture and farming together with urban and industrial settlements). Here it often occurs that N inventories at the regional scale do not fully match the distribution of nitrates in groundwater, highlighting the need to take into account processes occurring below the surface and within the aquifers. In these situations, the use of an isotopic approach to apportion the contribution of the different nitrate sources to aquifer contamination and to depict the processes governing accumulation and reduction is crucial for stakeholders to implement effective management actions. To achieve this overall objective, a compilation, in a comprehensive database, of all the available hydrochemical and isotopic data, has been performed. This dataset has been integrated with some unpublished data to fill the knowledge gaps in given areas or situations. The interpretation at the watershed scale of data obtained in local scale studies of groundwater hosted in a variety of sedimentary environments allows for the definition of the more relevant processes governing nitrate contamination in Northern Italy with the objective of assisting regulators in devising remediation strategies. This comprehensive picture provides a cost-effective methodology to screen the areas where isotope analyses can be applied, drawing on generally available statistical and groundwater monitoring data.

## 2. Study area

Northern Italy is characterized by a large alluvial valley comprising the Po and the Veneto plains, bordered by the Alpine and Apennine chains to the N and the S, respectively, and by the Adriatic sea to the E (Fig. 1). The total surface of the Po and Veneto plains is about 100,000 $km^2$. The Po river, 675 km long, collects the water of 141 tributary rivers from both Alpine and Apennine chains, while the Adige (410 km) and the Tagliamento rivers (170 km) collect 18 relevant tributary rivers from the Eastern Alpine belt. Regions hosting significant plain areas in Northern Italy are (from W to E) Piedmont, Lombardy, Veneto, Emilia Romagna and Friuli Venezia Giulia. More than 50% of the Italian Gross National Product is produced in Northern Italy, which hosts more than 20 million inhabitants. About one half of total surface is devoted to agriculture and to animal breeding, including mostly cattle, pigs and chickens.

The climate in the western sector is classified as temperate continental, with mean annual temperature of ~13°C, cold winters (in January, mean minimum and maximum temperatures of ~ -3° and +3°C) and hot summers (in July, mean minimum and maximum temperatures of ~16° and

~30°C). In the eastern sector, the continental climate is less accentuated due to the effect of the Adriatic sea (Cati, 1981): the mean annual temperature is ~ 14 °C, with mean minimum and maximum temperatures of ~ 0° and ~7°C in January, and of ~19° and ~27°C in July, respectively (Brancucci, 2001). Rainy periods are concentrated in spring and autumn, with mean annual rainfall in the range of 501-750 mm in the low plain and of 751-1000 mm in the high plain areas (Fratianni and Acquaotta, 2017). The relative humidity is high, due to intense evapotranspiration (Elmi et al., 2013).

The Po and the Veneto plains were generated during Quaternary by the dismantling of the Alpine and Apennine chains, mostly constituted by crystalline basement rocks (Western Alps), and their sedimentary (mostly marine) covers. This large sedimentary basin was significantly affected by subsidence in post-Oligocenic periods. Recent continental deposits were deposited during the Lower-Upper Pleistocene to Holocene. The total thickness of Quaternary sediments can reach about 0.5 km, being bounded at the bottom by Pliocenic sediments saturated by fossil salty waters in large parts. Coarse sediments generated by rock erosion due to tributaries of the Po river are located at the foothills of mountain belts, while finer sediments like sand, silt and clay have been transported by the Po river towards the sea. Alluvial sediments become progressively finer towards the centre of the plain and in correspondence with the river deltas along the Adriatic sea coast. A block diagram illustrating the geological and hydrogeological settings of the study area is reported in Fig. 1.

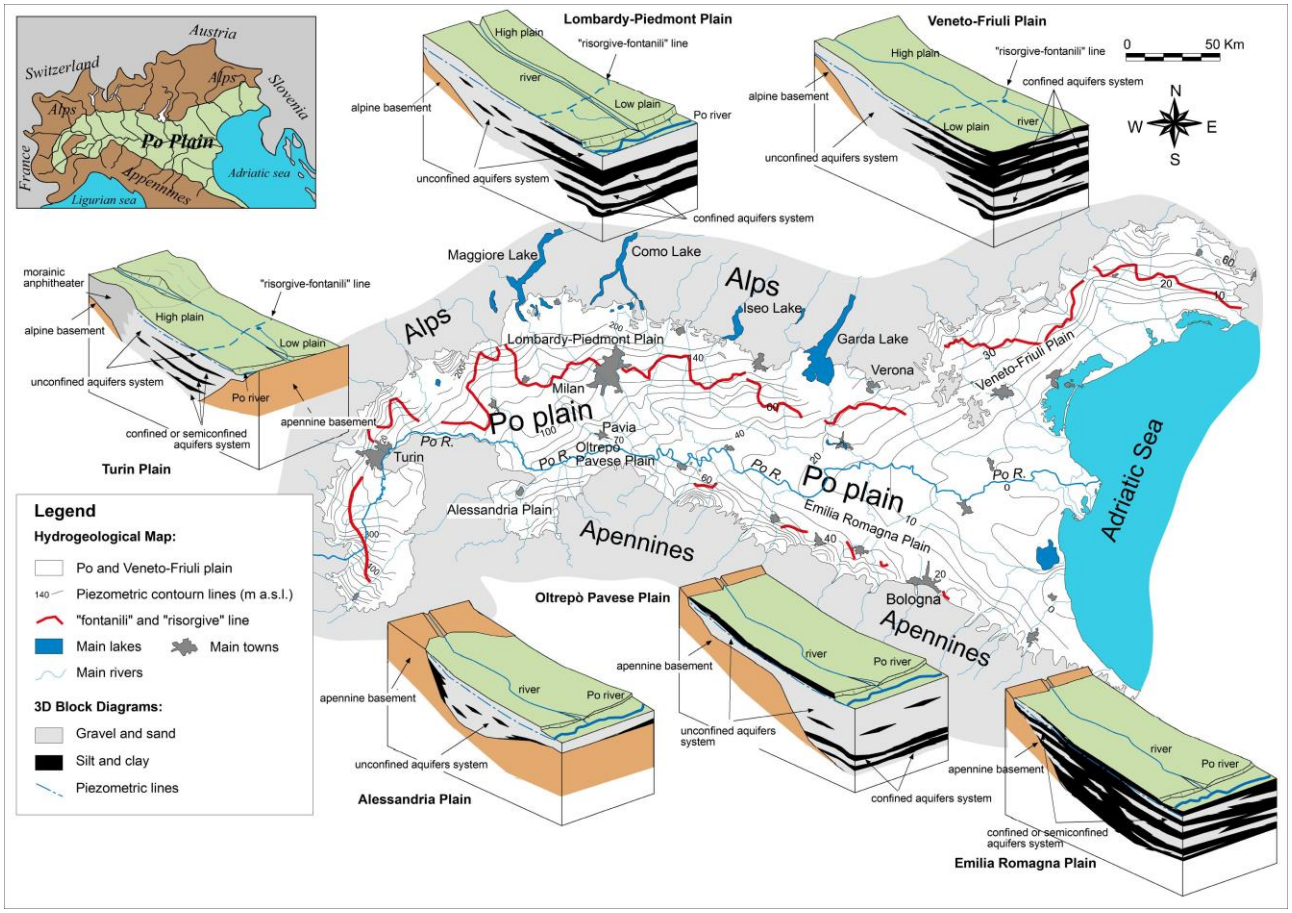


Fig. 1 – Location, simplified geological and hydrogeological settings of the investigated area. Piezometric contour lines from Giuliano et al. (1998), modified.

### *2.1 Hydrogeological setting*

The aquifer system in the investigated area mostly consists of multilayer aquifers constituted by gravel and sand layered with silt and clay. The shallow aquifers are generally unconfined while the deeper aquifers are semiconfined and confined. Unconfined aquifers are usually poorly connected with underlying aquifers in the low plain areas, characterized by a greater presence of fine sediments, while evidence of the effective connections among shallow and deep aquifers are found in alluvial fan areas, characterized by coarser sediments. The thickness of this aquifer system ranges from a few dozen meters to several hundred meters. At different depths, depending on the geographic position, a fresh-salt water interface is present, separating fresh- from deeper salt-groundwaters. This is of great importance, as it corresponds to the lower boundary of freshwater aquifers that are potentially exploitable for drinking, municipal and farming purposes.

The piezometric map of the shallow aquifer (Fig. 1) derives from regional studies (e.g. for the Piedmont plain) and piezometric levels recorded by the Regional Environmental Protection Agencies (ARPAs).

195 The groundwater flow in the unconfined aquifer is directed towards the Po River (i.e. roughly
196 oriented N–S in the pre-alpine sector and S–N closer to the Apennines). In the central western
197 sector, the flow is strongly controlled by the draining action of the Po river and its tributaries,
198 whereas, in the eastern sector, the Po river is not in hydraulic connection with groundwater.

199 The higher hydraulic gradients are registered close to the Alpine and Apennine chains in alluvial
200 fan areas (high plain). Typical hydraulic gradients of these areas vary from 8‰ to 10‰ in
201 Piedmont, and from 4‰ to 8‰ in the other areas of the Po and the Veneto-Friuli high plain.
202 Lower hydraulic gradients characterize low plain aquifers along the Po river (normally ranging
203 from 1‰ to 4‰); in the central-eastern part of the Po Valley they decrease to values of 0.2‰-
204 1‰. At the transition from the high to low plain, the decrease in the hydraulic gradient is generally
205 associated to the emergence of typical lowland springs (fontanili) (Fig. 1) (Minelli et al. 2002;
206 Vorlicek et al. 2004; De Luca et al. 2009, 2014; Zini et al. 2011; Balderacchi et al. 2016; Fumagalli et
207 al. 2017). The highest hydraulic conductivity ($1\text{-}10 \cdot 10^{-3}$ m/s) is measured in alluvial fan areas,
208 whereas lower values ($1\text{-}10 \cdot 10^{-5}$ m/s) are measured in low plain areas, although some areas
209 characterized by relatively high permeability coefficients have been identified in the western and
210 the central sectors of the low plain. The water level depth in shallow aquifers is highly variable in
211 the Po plain: minimum values of 1-5 m b.g.l. are recorded in the central part of the plain, whereas
212 closer to the Alps it may reach 30-50 m, and close to the Apennines it is set around 10 m.

213 Shallow aquifers and aquifers located in alluvial fans are characterized by relatively high intrinsic
214 vulnerability values, while deep aquifers and shallow aquifers characterized by fine sediments in
215 the unsaturated zone show lower vulnerability.

216

217 ***2.2 Groundwater nitrate contents and infiltrability***

218 The existing relationship between the characteristics of the unsaturated zone in the subsoil and
219 groundwater nitrate contents is shown in Fig. 2. The regional infiltrability map was developed
220 through the joint processing of the shallow aquifer textures (gravel, sand and silt) and the
221 thickness of the surface alteration layers and/or loess deposits (Giuliano et al., 1998). Basically, the
222 infiltration parameter, used at regional level, facilitates the identification of those areas where it is
223 easier for substances coming from the surface (in our case, nitrates) to be hydro-transported by
224 recharge waters to the unconfined aquifers.

225 The plain sector is represented in different colors according to the classification of infiltrability
226 (very high, high, medium, low or negligible). The location of the wells periodically sampled by the
227 ARPAs is also indicated and differentiated based on their nitrate content (lower or higher than 50
228 mg/l, the regulatory limit for drinking water supplies). High values are observed in areas
229 characterized by high infiltrability, mostly at the Alpine and Apennine foothills. This is of particular
230 concern since these areas represent the recharge areas for all the Po valley aquifer systems. On
231 the other hand, large portions of the western and central plain (e.g. South of Milan) showing high
232 infiltrability values do not record high nitrate concentrations in groundwaters. However, it should
233 be noted that the ARPA network also considers some wells tapping in semi-confined and confined

aquifers, where the nitrate concentrations are obviously lower because of the higher protection offered by the overlying low-permeability layers. Nonetheless, in large portions of the central plain, nitrate concentrations do not exceed 50 mg/l in the unconfined aquifer (Pilla et al., 2006; Guffanti et al., 2010), indicating that the aquifer grain size (i.e. the hydraulic conductivity) and the thickness of the surface alteration layers are not the only parameters governing the contamination levels.

Previous studies have indicated that nitrate concentrations in aquifers could depend on different physical-chemical processes. High nitrate contents have been found in areas with high infiltration and/or low aquifer dilution capacity. On the other hand, low nitrate contents have been observed in areas with high dilution capacity, lower infiltration rates from the surface and/or in the presence of enhanced denitrification processes (Debernardi et al. 2008; Lasagna et al. 2013; Lasagna et al. 2016b).

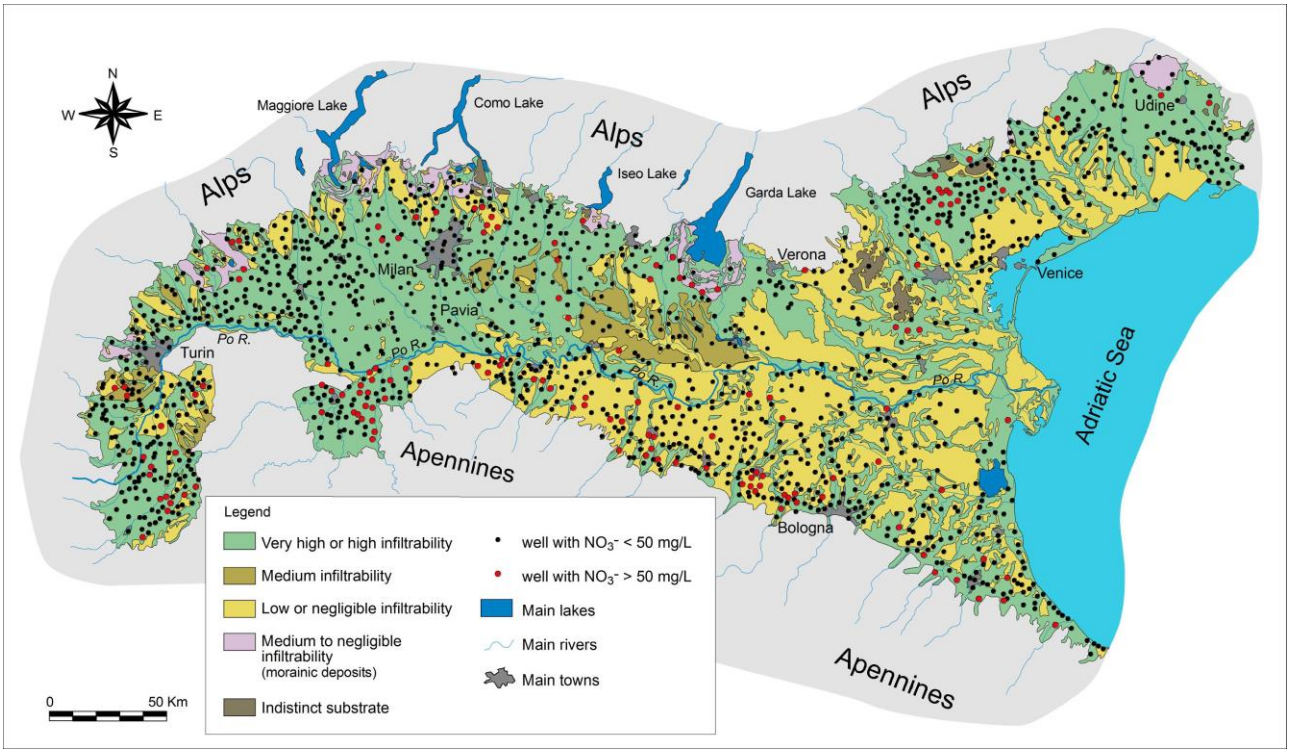


Fig.2 - Infiltrability map of the Po, Veneto and Friuli plain (after Giuliano et al., 1998, modified). Dots represent wells periodically sampled by regional environmental protection Agencies. Black dots = nitrate concentration <50 mg/l; red dots = nitrate concentration >50 mg/l.

### *2.3 Nitrate Vulnerable Zones from agricultural sources*

The Nitrates Directive was applied in Italy by national legislation (Decree Law 152/99) and the NVZ designation was undertaken under the competence of the Regional Authorities. The first NVZ designation took place in the late nineteen-nineties, based on the results of monitoring programmes assessing nitrate concentration in surface and groundwaters, and the trophic status of surface waters, and the NVZs were enlarged in different steps between 2000 and 2011.

These enlargements were performed in Italian Regions by means of different approaches, and based on multiple parameters (e.g. intrinsic vulnerability of the shallow aquifer obtained with different methods, N-surplus, and soil attenuation capacity). Consequently, these delimitations were performed with a forward-looking approach.

The total designated NVZs in Piedmont, Lombardy, Veneto, Friuli Venezia Giulia and Emilia-Romagna represent almost 70% of designated NVZs in Italy (Fig. 3); moreover, they represent a percentage ranging between the 50% and 60% of regional plains areas (Ministry for Environment, Land and Sea, Ministry of Agriculture, Food and Forestry Policies, regions of Piedmont, Lombardy, Veneto, Emilia-Romagna and Friuli Venezia Giulia, 2010). In the NVZs, action programmes are to be implemented by farmers on a compulsory basis, including curbs on fertilizer application (mineral and organic) and other measures at farm scale. The costs of these measures in the framework of farm economics can have a negative economic impact, especially for small farm holdings (ADAS, 2011).

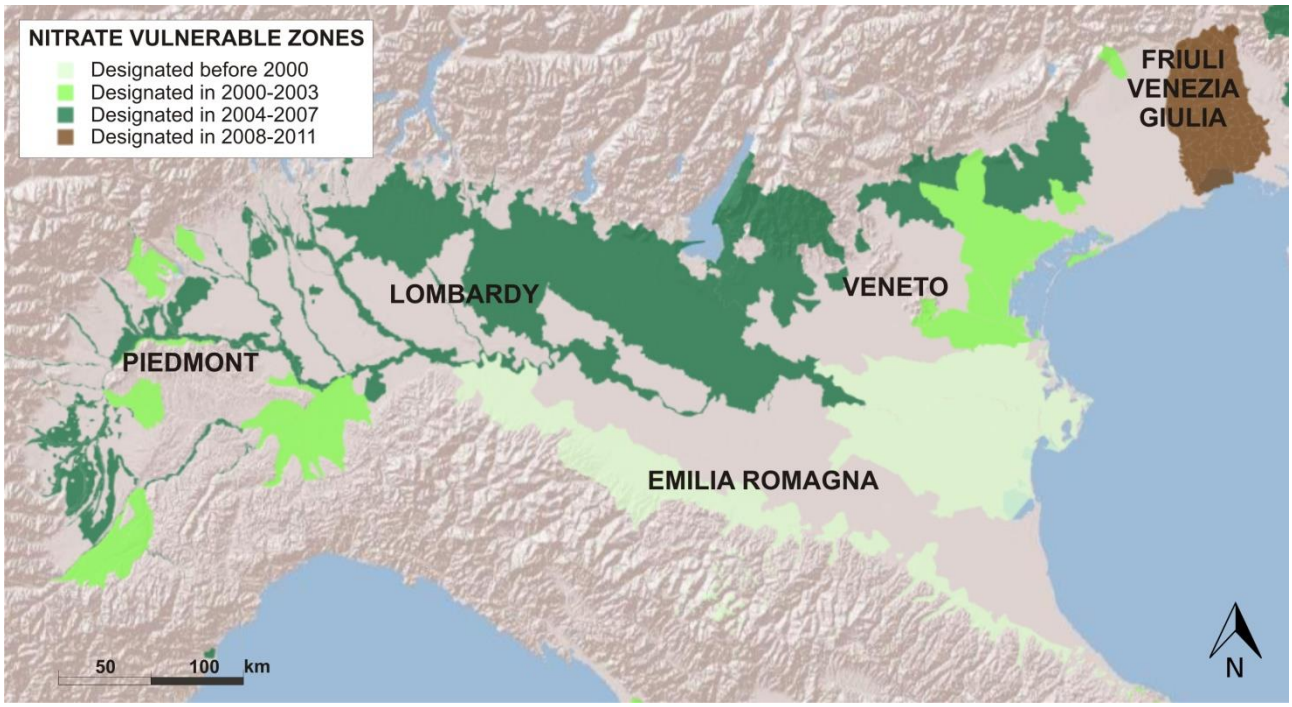


Fig. 3 – NVZs of Northern Italy (map elaborated with http://fate-gis.jrc.ec.europa.eu/geohub/MapViewer.aspx?id=2)

## 3. Materials and methods

The compiled database is made up of hydrochemical and isotopic data, retrieved from national and international publications (Pilla et al., 2005; 2006; 2007; Lasagna et al., 2006; 2015; 2016a, 2016b; Debernardi et al., 2008; Guffanti et al., 2010; Sacchi et al., 2013; Saccon et al., 2013; Martinelli et al., 2014a), conference proceedings (Dadomo and Martinelli, 2005; Arduini et al.,

2007; Sacchi et al., 2007; Martinelli et al., 2014b; 2014c) and unpublished reports (Provincia di Verona, 2001; ISO4, 2005). These data were all determined in water extracted from shallow aquifers during a single campaign. Only in few exceptions groundwater monitoring involved repeated sampling of the same well (Provincia di Verona, 2001; Sacchi et al., 2007; Saccon et al., 2013). As in many instances this monitoring evidenced a seasonal evolution of both nitrate concentrations and isotopic compositions, all these data were treated as if they were individual measurements to avoid the issue of representativeness. Unfortunately, not all the groundwater samples have a correspondingly complete chemical analysis.

All the data sources are clearly identified in Tab. S1 (Supplementary material), allowing us to refer to the publication in terms of the analytical techniques used. Nitrate isotope data were produced using the silver nitrate method (Silva et al., 2000) or the bacterial denitrification method (Sigman et al., 2001), and results are expressed in the standard $\delta^{15}N_{NO3}$ ‰ vs AIR and $\delta^{18}O_{NO3}$ ‰ vs SMOW notation. Boron isotopes were determined by MC-ICP-MS, with results expressed as $\delta^{11}B$‰ with respect to the NBS-951 standard. The database is a compilation of results generated in different laboratories, at different times and by different techniques, and no data are available that can be used for inter-laboratory comparison. Nevertheless, isotopic compositions are always expressed with respect to international standards, and therefore, assuming that each laboratory has correctly implemented the analytical protocol, the results should, in principle, be comparable.

To fill in the knowledge gaps in given areas (e.g. the Parma province in Emilia Romagna) or situations (e.g. the $\delta^{11}B$ composition of some compositional end-members), additional original analyses were also performed and reported in Tab. S1 (Supplementary material) and Tab. 1. For these samples, nitrate isotopes were determined by IRMS at ISO4, Italy. Samples were prepared and purified according to the method described by Silva et al., 2000. Uncertainties ($1\sigma$) are $\pm$0.5‰ for $\delta^{15}N_{NO3}$ and $\pm$1‰ for $\delta^{18}O_{NO3}$. Boron isotope ratios in purified fractions of groundwaters were measured by MC-ICP-MS Neptune Plus at ALS Scandinavia AB, Luleå (Sweden), with an uncertainty of $\pm$0.4 to $\pm$1‰, using a combination of internal standardization and bracketing standards for instrumental mass bias correction. Boron isotopes of relevant anthropogenic sources for the study area (e.g. pig manure, sewage, synthetic fertilizer) were determined by positive TIMS on $Cs_2B_4O_7$ deposited on the ion source filament with graphite and mannitol, which produces $CsBO_2$ ions, after boron purification through ion exchange resins (Tonarini et al., 1997). Analyses were performed at CNR-IGG in Pisa (Italy) using a VG Micromass 54 E mass spectrometer with an uncertainty of $\pm$0.5‰, calculated on replicate analyses of the NBS-951 standard.

The location of samples included in the database is shown in Fig. 4, with different color codes corresponding to the regions. The distribution of sampling points mostly reflects the areas where nitrate concentrations in groundwater sometimes exceeded the regulatory limits.

To test the possible correlations of the isotopic composition with anthropogenic pressure indicators, data were aggregated by province and the descriptive statistical parameters were calculated (Min, Max, Mean, Median; Tab. S2 in Supplementary material). Farm census data (number of cattle, number of pigs and Utilized Agronomical Area [UAA] per province) for the year

2010 were obtained from the National Statistical Institute (ISTAT, 2010), while the number of inhabitants and population density were retrieved from the ISTAT database (year 2009).

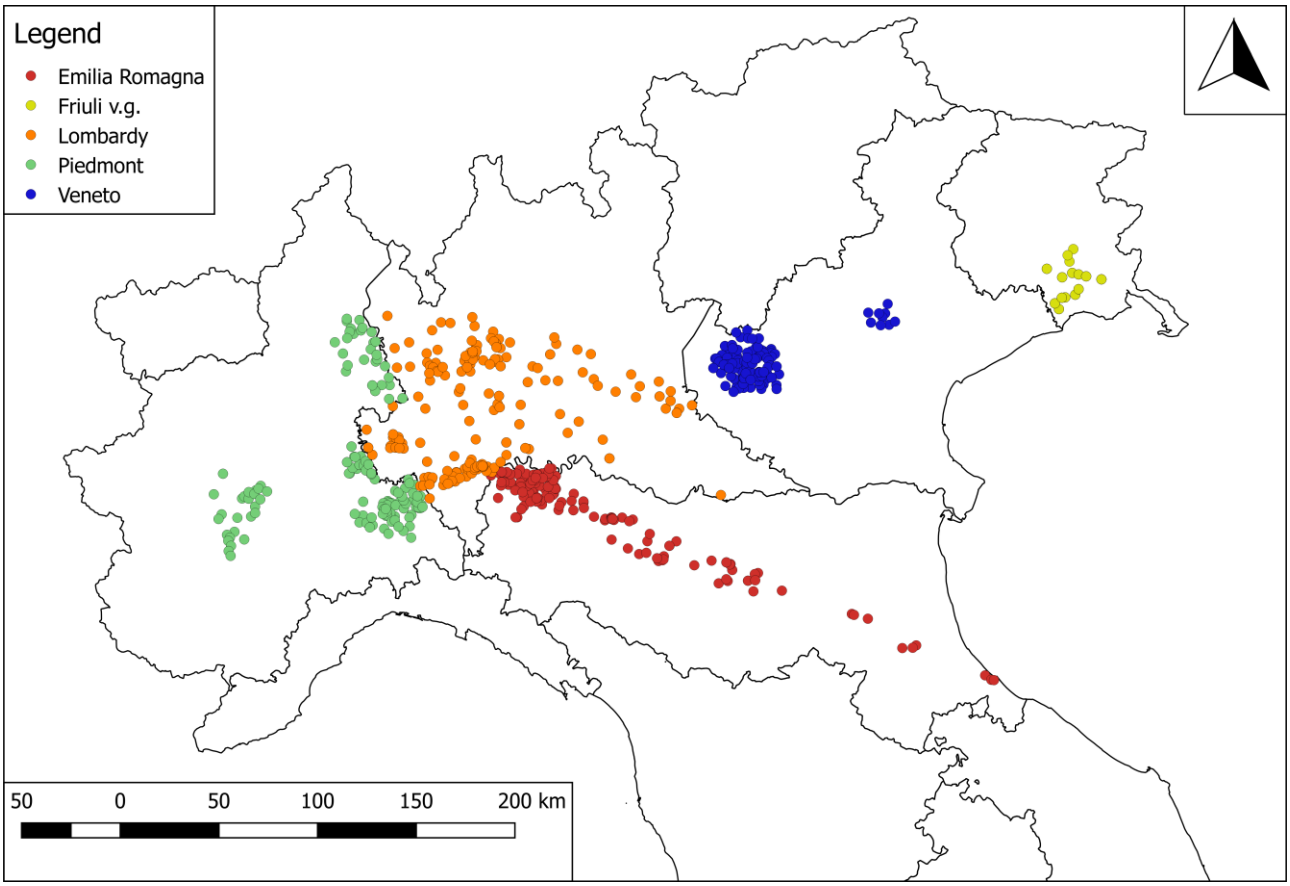


Fig. 4 - Location of samples included in the hydrochemical and isotopic database. Colors correspond to the different regions.

## 4. Results and discussion

### *4.1 Groundwater hydrochemistry*

Previous studies have indicated that in the Po plain, most of the waters hosted in alluvial fans of the Alpine and Apennine chains show a Ca(Mg)-$HCO_3$ facies, and TDS ranging from 300 to 3500 mg/l. Groundwaters with a Na(K)-$HCO_3$ (TDS range=500-2700 mg/l) facies subordinately occur in the eastern part of the Po plain, characterized by fine sediments. This change in the chemical composition is due to Na-Ca exchange with clays. Ca(Mg)-$SO_4$ groundwaters (TDS range=750-2400 mg/l) occur in limited areas at the foothills of the Apennine chain and are the result of interaction between meteoric waters and evaporitic minerals of Triassic and Messinian age (Giuliano, 1995; Martinelli et al., 2014a). Na (K)-Cl groundwaters (TDS range= 1200-2000 mg/l) occur in the central and eastern part of the Po river plain. They are the result of interactions between meteoric waters

and evaporitic layers formed during Quaternary transgressive episodes (Conti et al., 2000; Pilla et al., 2010; Martinelli et al., 2016).

Ca(Mg)-$HCO_3$ groundwaters and Ca(Mg)-$SO_4$ groundwaters are hosted in unconfined and semi-confined coarse sediment aquifers characterized by relatively high flow velocities (0.1-5 m/day). They are often affected by a significant nitrate contamination (50-100 mg/l) (Pilla et al., 2006; Sacchi et al., 2013; Martinelli et al., 2014c). Na(K)-$HCO_3$ and Na(K)-Cl groundwaters are hosted in confined fine sediment aquifers characterized by low groundwater flow velocities (less than 10 m/yr), which inhibit pollution phenomena.

Groundwater hydrochemical data, when available in the database (Tab. S1; Supplementary material), were represented in the classical Piper diagram (Fig. 5). Most of the samples fall within the field of Ca-$HCO_3$ facies with medium TDS values, reflecting water circulation in shallow unconfined aquifers. In areas where the marine substratum is closer to the surface (Fig. 1), the groundwater composition is affected by a contribution of Na-Cl waters.

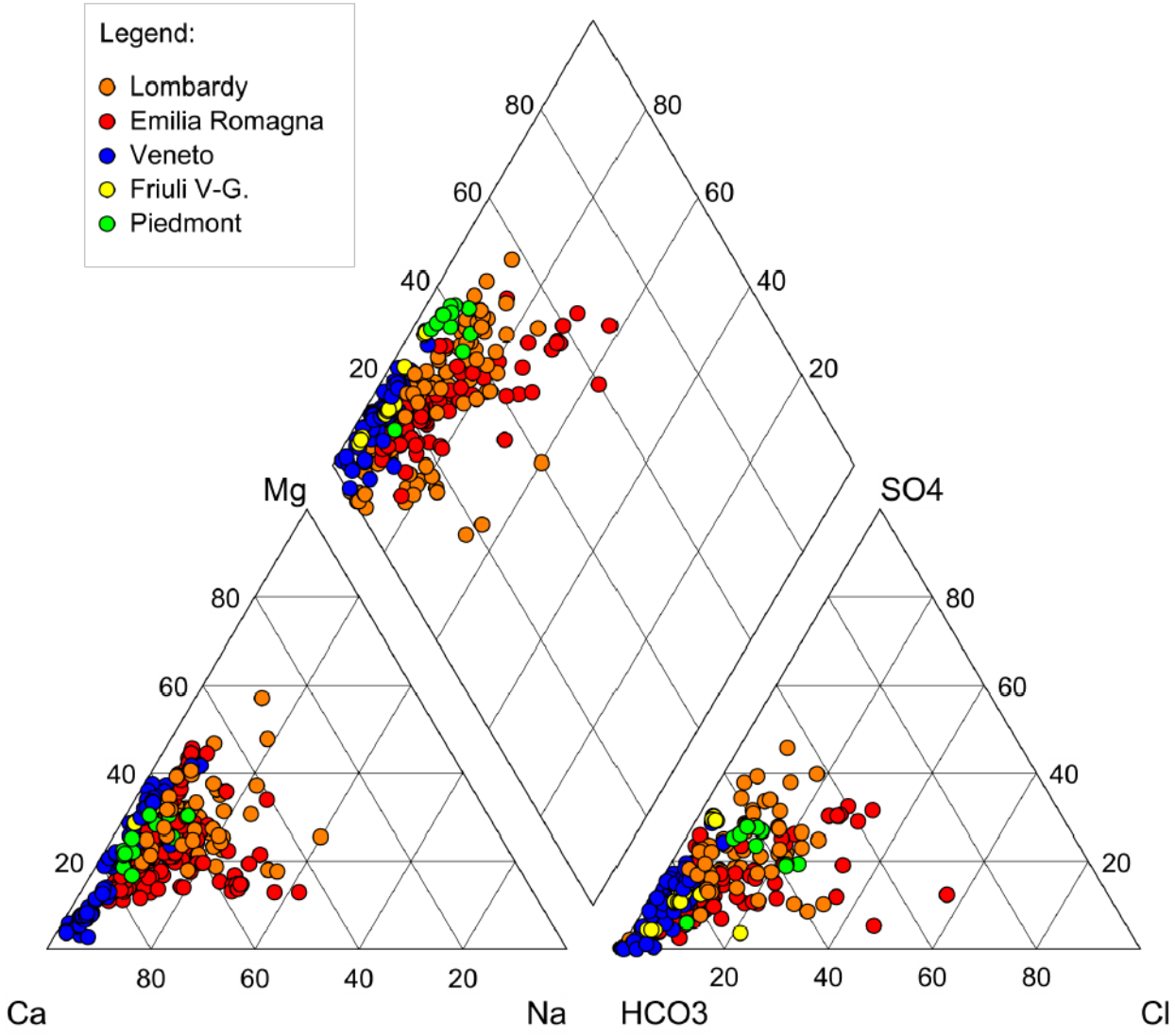


Fig.5 - Piper diagram showing the available compositions of groundwaters.

Groundwater TDS values in the studied area are strongly determined by mineralogical composition of the substratum, being higher in the eastern and southern parts due to the higher relative abundance of carbonates in the aquifer matrix. The relationship between groundwater TDS and nitrate contents is shown in Fig. 6. The plot evidences that the higher nitrate concentrations are often found in low TDS waters, mostly hosted in alluvial fans of the Piedmont-Lombardy plain (Fig.1). Since TDS is expected to increase with time due to mineral weathering, this could indicate a more recent recharge and a faster circulation in these aquifers. Nevertheless, also high TDS (≥ 1000 mg/l) waters in the lower Lombardy and Emilia-Romagna plain show non-negligible nitrate concentrations (~ 30 mg/l), confirming a contribution of present-day recharge for these waters, and suggesting that the differences in groundwater age in unconfined aquifers throughout the investigated area should be relatively small.

An alternative explanation for the nitrate-TDS relationship considers that microbial oxidation of ammonium generates acidity along with nitrate in soils, that is readily buffered by the dissolution of carbonates from the aquifer matrix, if these are present (Spruill et al., 2002). The relationship between groundwater nitrate concentrations and hydrochemistry has been recently reviewed by Menció et al. (2016) who demonstrated, in aquifers characterized by different lithologies, that nitrates have an enhancing effect upon the biogeochemical processes that control water-rock interactions. This generally leads to an increase in major ions concentrations (therefore in TDS values), but also homogenizes the overall hydrochemistry despite lithological differences, and enhances or reduces the geochemical processes that control groundwater composition at equilibrium. This could be the reason why no clear correlation between nitrate and calcium contents could be observed in groundwater from the investigated area, suggesting that other natural processes may mask this relationship (e.g. cation exchange, gypsum dissolution etc.).

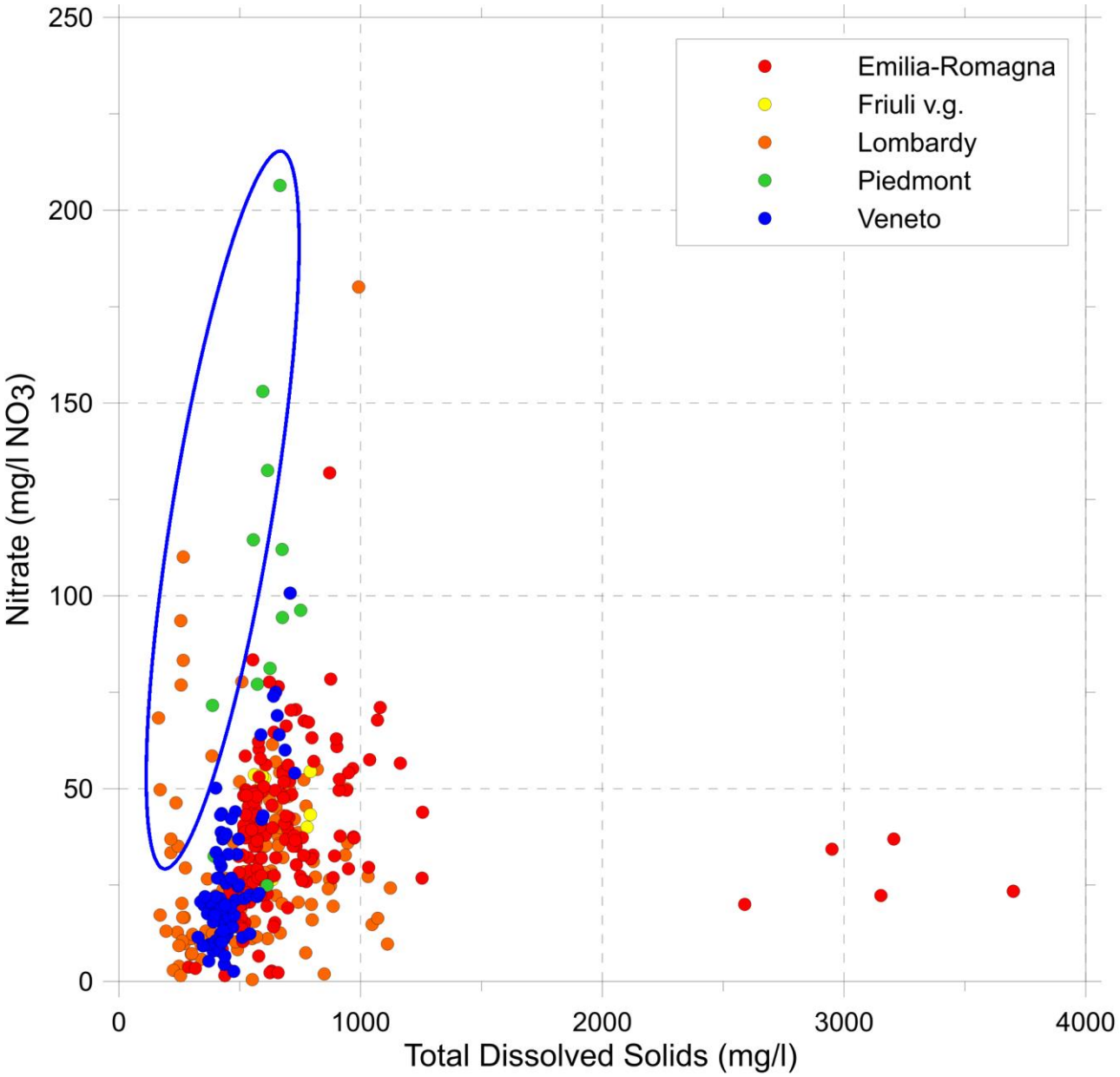


Fig. 6 –Total Dissolved Solids vs nitrate concentrations of selected groundwaters. The higher nitrate concentrations are often found in low TDS waters (blue oval).

### *4.2 Nitrate sources*

Atmospheric deposition measured in Northern Italy accounts in average for 20-25 kg N $ha^{-1}$ $yr^{-1}$ (Rogora et al., 2012). While this represents an important source of reactive N for surface waters, it is a minor component of the total N input to soils compared to agricultural and civil or industrial inputs (EEA, 2005), as indicated by N budgets calculated in several watersheds within the Po river basin (e.g. Bartoli et al., 2012). As most isotopic studies targeted areas with high nitrate concentrations, often located close to the Alpine and Apennine chains (Fig. 2 and Fig. 4), we can reasonably assume to a first approximation that denitrification processes are not very relevant in

the study area (see also section 4.3). Therefore, the N isotopic composition should be mostly determined by the source of dissolved nitrates.

The $\delta^{15}N$ values recorded in the database vary between -7.84 and +37.50‰ vs AIR (n=818). A frequency histogram (Fig. 7) shows that the more common values in groundwater range between +6 and +8‰. These values correspond to the isotopic compositions of nitrates naturally generated by the degradation of the soil organic matter (Kendall et al., 2007). Nevertheless, the nitrate concentrations recorded often largely exceed the expected natural background level (~5 mg/l, Edmunds and Shand, 2008), suggesting that this isotopic value derives from anthropogenic sources, namely from the mixing between synthetic sources and organic matter-derived nitrates.

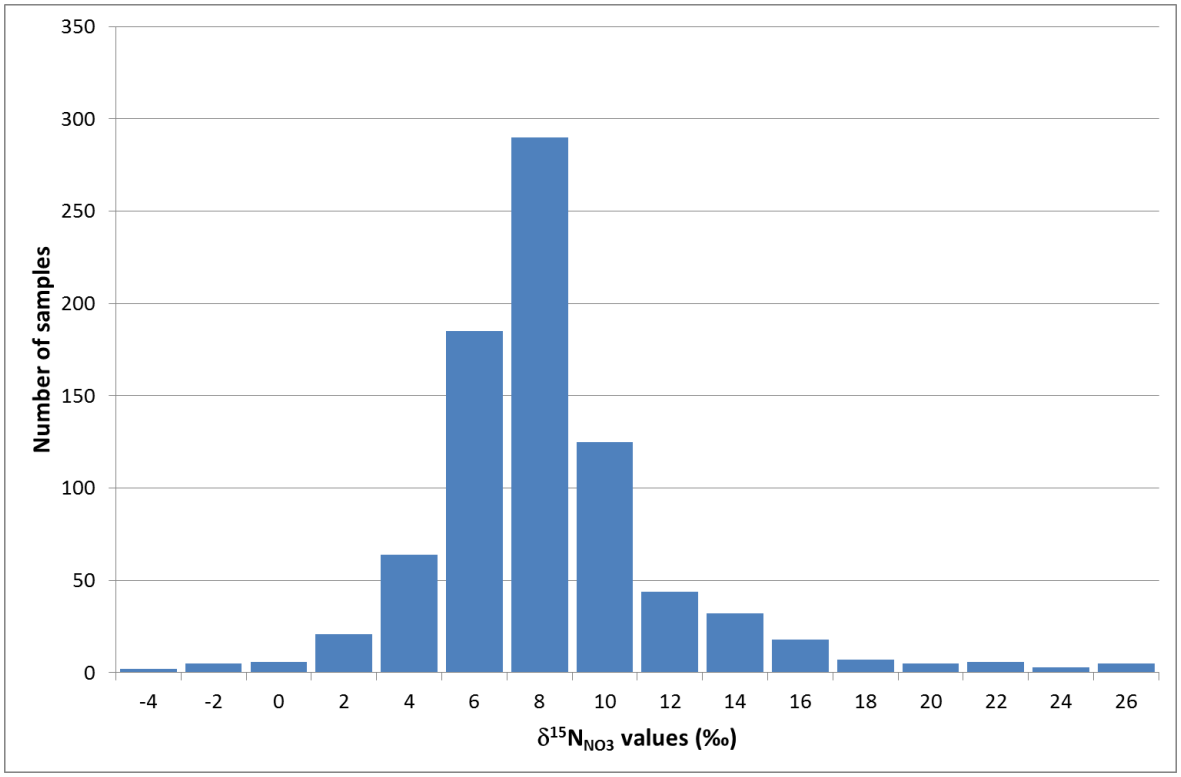


Fig. 7 – Frequency histogram of $\delta^{15}N_{NO3}$ values in groundwater. Values on the x-axis represent the interval's upper limit.

The distribution of $\delta^{15}N$ was compared to nitrate concentrations, in order to identify the source(s) that mostly contribute to the observed contamination. Two data modes are present (evidenced by ovals in Fig. 8): one with a relatively depleted value ($\delta^{15}N$ of about +2‰) corresponding to synthetic sources (i.e. fertilizers) and mostly evident in the Piedmont region, and a second, wider mode, around +8‰, displayed by samples from different regions. More interestingly, high nitrate concentrations are mostly recorded in samples with very enriched $\delta^{15}N$, suggesting that these derive from organic matter sources. This is in contrast with the $\delta^{15}N$ distribution observed in the sole Lombardy plain (Sacchi et al., 2013), where both depleted and highly enriched values were mostly characterized by low nitrate concentrations, the former attributed to synthetic sources and the latter due to the influence of denitrification phenomena.

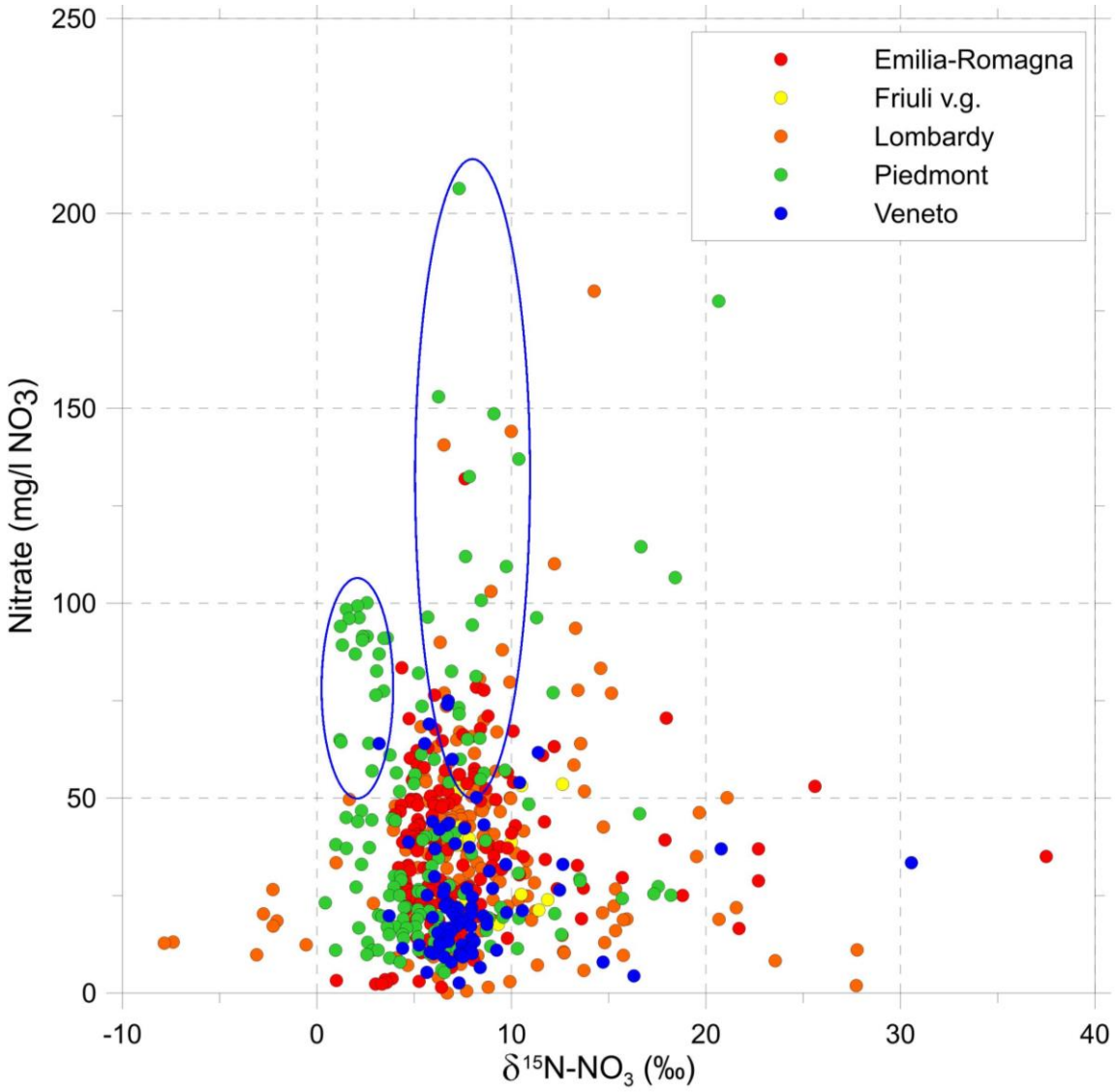


Fig. 8 – Nitrate concentrations versus $\delta^{15}N$ values in groundwaters. Blue ovals evidence the two different modes (see text for explanation)

In a pioneering study for Italy, Dadomo and Martinelli (2005) in the Piacenza province (Emilia-Romagna) found a relationship between the distribution of $\delta^{15}N$ values and the location of pig farms in the area. In order to check whether a similar correlation could be observed at the basin scale, statistical parameters were calculated for each province in the investigated area (Tab. S2; Supplementary material) and compared to farm census and population data. All possible correlations between $\delta^{15}N$ values and anthropogenic pressure indicators were considered. At the basin scale, a significant correlation between the median $\delta^{15}N$ values and the number of pigs per UAA is observed (n=25; r= 0.478; p=0.015), as shown in Fig. 9, whereas no significant correlations could be observed for cattle density, cattle + pig density or population density (Tab.S2; Supplementary material). This correlation with pig density, although significant, is not very strong, due to some limitations imposed by the dataset, and by the adopted model (linear correlation rather than exponential). Nevertheless, it should be noted that the provinces with the highest pig

densities (i.e. Bergamo, Brescia and Mantua) are poorly correlated with the others. This could be due, on one hand, to the low amount of available isotopic data for these provinces, but also to the fact that, if denitrification is not occurring, the $\delta^{15}N$ enrichment would be limited to the highest $\delta^{15}N$ values displayed by the contamination source (for example, in the case of pig manure, limited to 16‰, according to Vitòria et al. (2008)). In other words, although the total number of pigs may increase, the $\delta^{15}N$ content may be constant if it presents the same origin. If these three provinces are eliminated from the plot, the correlation significantly improves (Fig. 9), and the correlation with the total number of pigs also becomes significant ($p<0.01$), whereas those with cattle or population remain non-significant.

A correlation between animal husbandry, and particularly with the number of pigs, and groundwater nitrate contamination has been observed elsewhere (e.g. Aquilina et al., 2012; Boy-Roura et al., 2013), and may be due to the fact that the produced type of excrement is often a slurry rather than manure (Lorimor et al., 2004; Mantovi et al., 2006; Risberg et al., 2017). Nevertheless, $\delta^{15}N$ values could also be enriched due to denitrification, a process that, in absence of $\delta^{18}O$ data, cannot be ruled out.

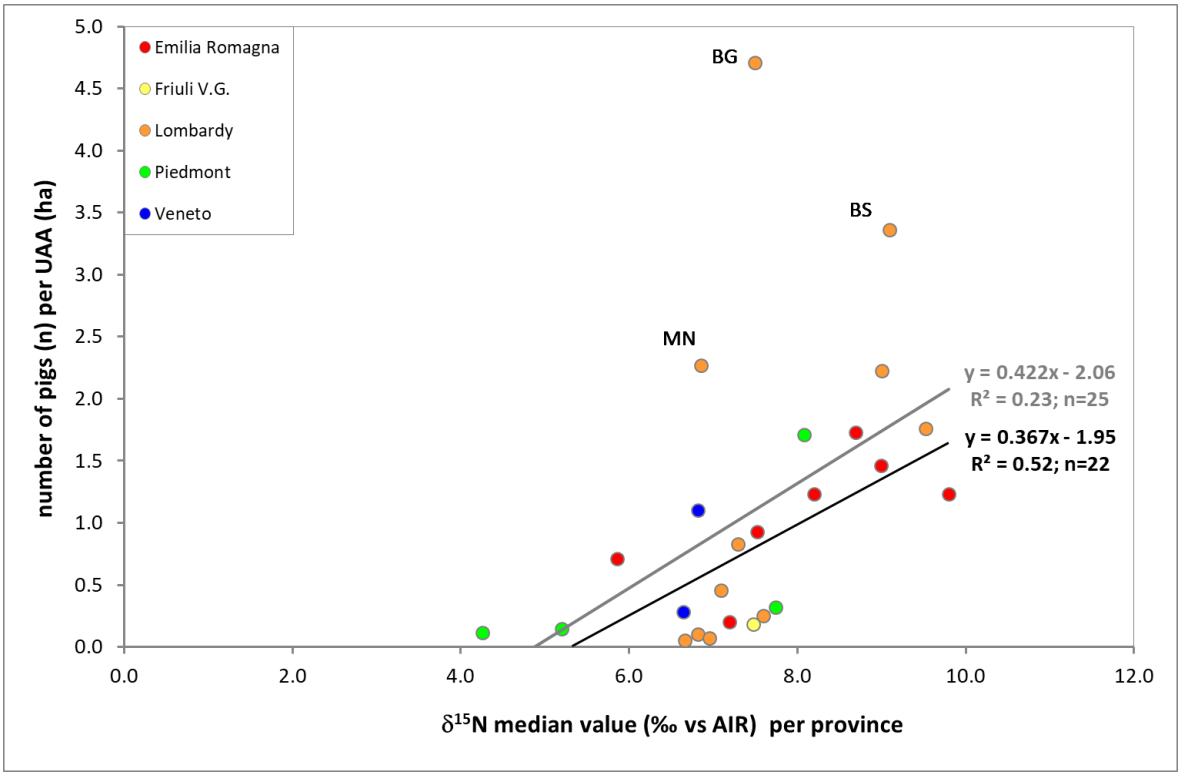


Fig. 9 – Number of pigs per UAA versus $\delta^{15}N$ median values calculated per each province. Grey line = all data; black line = excluding the Bergamo (BG), Brescia (BS) and Mantua (MN) provinces.

### *4.3 Processes affecting nitrate contents*

The $\delta^{18}O_{NO3}$ values recorded in the database vary between +1.08 and +25.5‰ vs SMOW (n=412). A frequency histogram (Fig. 10) shows that the more common values in groundwater range between +4 and +10‰.

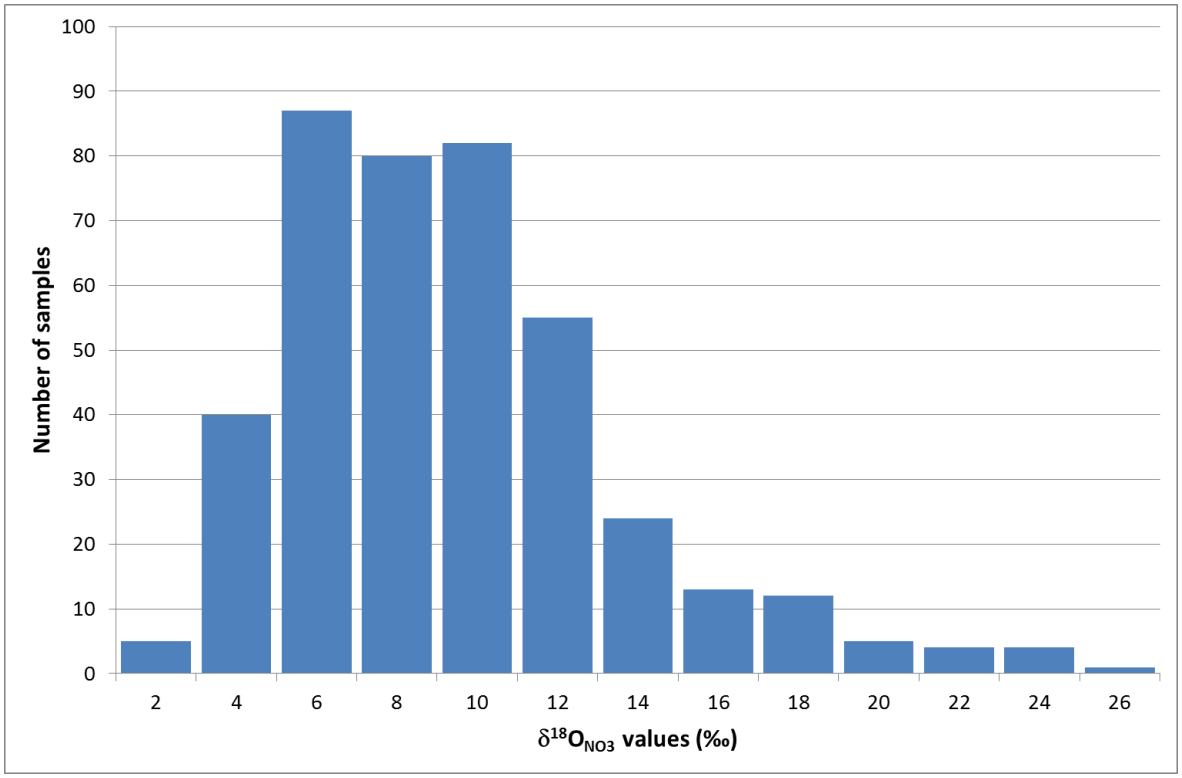


Fig. 10 – Frequency histogram of $\delta^{18}O_{NO3}$ values in groundwater. Values on the x-axis represent the interval's upper limit.

Results were plotted on the classical $\delta^{18}O_{NO3}$ vs $\delta^{15}N_{NO3}$ diagram (Fig.11), reporting the expected range of isotopic composition for the different sources. These were derived from the literature (Clark and Fritz, 1997; Kendall et al., 2007), and confirmed by some $\delta^{15}N_{NO3}$ values determined locally and reported in Saccon et al. (2013) and Sacchi et al. (2013). The lowest values of $\delta^{18}O_{NO3}$ of the potential sources are calculated, considering that in the nitrate molecule one oxygen atom is provided by atmospheric oxygen ($\delta^{18}O_{O2}$≈+23.5‰) and two are provided by the water molecule (Kendall et al., 2007). Since the isotopic composition of precipitation falling on the plain sector ranges between -6 and -9‰ in $\delta^{18}O_{H2O}$ (Longinelli and Selmo, 2003), a fully equilibrated nitrate should then range between +1.83 and +3.83‰ in $\delta^{18}O_{NO3}$.

Two sets of samples characterized by enriched $\delta^{18}O_{NO3}$ can be observed in Fig. 11, one close to the compositional field of synthetic fertilizers, and one related to denitrification processes. The first set, compatible with the nitrification of synthetic fertilizers, accounts for a relatively low number of samples. This process produces nitrates that maintain the atmospheric $\delta^{15}N_{N2}$ signal (see discussion in the previous section 4.2), but are progressively more depleted in $\delta^{18}O_{NO3}$ due to the

incorporation of oxygen from the water molecules. Nevertheless, the $\delta^{18}O_{NO3}$ is slightly more enriched than expected for a full equilibration with $\delta^{18}O_{H2O}$. This enrichment is often observed in microbially-produced nitrate, and is attributed to many possible reasons (e.g. nitrification occurring in the soil, where the isotopic composition of the available water may be slightly enriched by evaporation), although the issue is still being debated (Kendall et al., 2007). The presence of isotopic compositions attributable to nitrification of synthetic fertilizers, although not so frequent, indicates a fast transfer of nitrates to groundwater, with a low residence time in soils, thus confirming for these cases the high permeability, infiltrability and intrinsic vulnerability of the aquifer.

On the other hand, isotopic compositions enriched due to denitrification are present in a relatively larger number of samples (≈ 90, corresponding to about 22% of the available data). According to Fig. 11, samples plot between two lines with a 0.5 $\delta^{18}O/\delta^{15}N$ slope, one with more enriched $\delta^{18}O_{NO3}$ values, originating from synthetic fertilizers, and the second from manure and septic system effluents. Hence, as both these nitrate sources are present in the area, they are both prone to denitrification when favorable environmental conditions are present. The observed isotopic enrichment (Fig. 11) allows for the consideration of denitrification as being responsible for nitrate abatement in groundwater affecting up to 70-80% of the original content, depending on the initial isotopic composition and the enrichment factor used (Kendall et al., 2007; Sacchi et al., 2013).

Denitrification was mostly reported in the lower plain of Piedmont and Lombardy (Pilla et al., 2005; Pilla et al., 2007; Debernardi et al. 2008; Guffanti et al., 2010; Sacchi et al., 2013; Lasagna et al. 2016b). Studies indicate that, under different soil and crop types, denitrification occurs when the water table is shallow, within 5 m from the surface, allowing the establishment of reducing conditions at shallow depths. This can occur naturally in low permeability soils, or as a consequence of flood irrigation adopted in rice cultivation. In other cases, denitrification was observed in shallow aquifers characterized by a low-permeability unsaturated zone. In Piedmont, a high denitrification rate was reported in areas with a shallow aquifer of limited thickness (e.g. Poirino Plateau) characterized by low permeability and low dilution degree. In this case, the nitrate input is not diluted in the aquifer, and high nitrate concentrations (even higher than 100 mg/l) are present in groundwater, despite the denitrification process.

Indirect evidence for ongoing denitrification can be obtained with hydrochemical tools, as these waters often contain detectable dissolved Fe and Mn contents. Both these metals are geogenic in origin (Maffei et al., 2005), as they derive from the dissolution of Fe(II)-Mn(II)-bearing minerals or the reduction of Fe-Mn oxyhydroxides present in the sediments. In the redox reaction sequence, $O_2$ reduces before nitrate which again is followed by reduction of Mn-oxides and by reduction of Fe-oxides (Appelo and Postma, 2005). Therefore, the presence of nitrates and of Fe/Mn is mutually exclusive. In the lower Lombardy plain, Sacchi et al. (2013) mapped groundwater samples with Fe and Mn concentrations above 100 and 50 µg/l respectively, as metals above these concentrations may be taken as indicators of reducing environments (McMahon and Chapelle, 2008; Wendland et al., 2008), and compared the distribution with that of nitrates. They concluded that in the low plain unconfined aquifers, the input of nitrates from the surface must have been

reduced by denitrification due to the presence of an anoxic environment. In other Regions (e.g. Veneto and Emilia Romagna) little isotopic evidence of the presence of denitrification is reported. This is due, on the one hand, to the lack of $\delta^{18}O_{NO3}$ values for these areas. On the other, it should be noted that most isotopic studies targeted areas with high nitrate concentrations, often located close to the Alpine and Apennine chains (Fig. 2 and Fig. 4); thus, the lower Veneto plain and the higher Emilia-Romagna plain have not been assessed. Nevertheless, the presence of dissolved Fe and Mn, often associated to $NH_4^+$ and As, is documented in unconfined aquifers of the low plain throughout the investigated area (e.g. Maffei et al., 2005). Therefore, based on the available hydrochemical and isotopic evidence (e.g. Rotiroti et al., 2014, 2017; Giambastiani et al., 2016; Petrini et al., 2014; Castaldelli et al., 2013; Carraro et al., 2013), the absence of nitrates in groundwater from the central Po plain can be reasonably ascribed to denitrification, whereas the main factor promoting this permanent loss of reactive nitrogen is the shallowness of the water table.

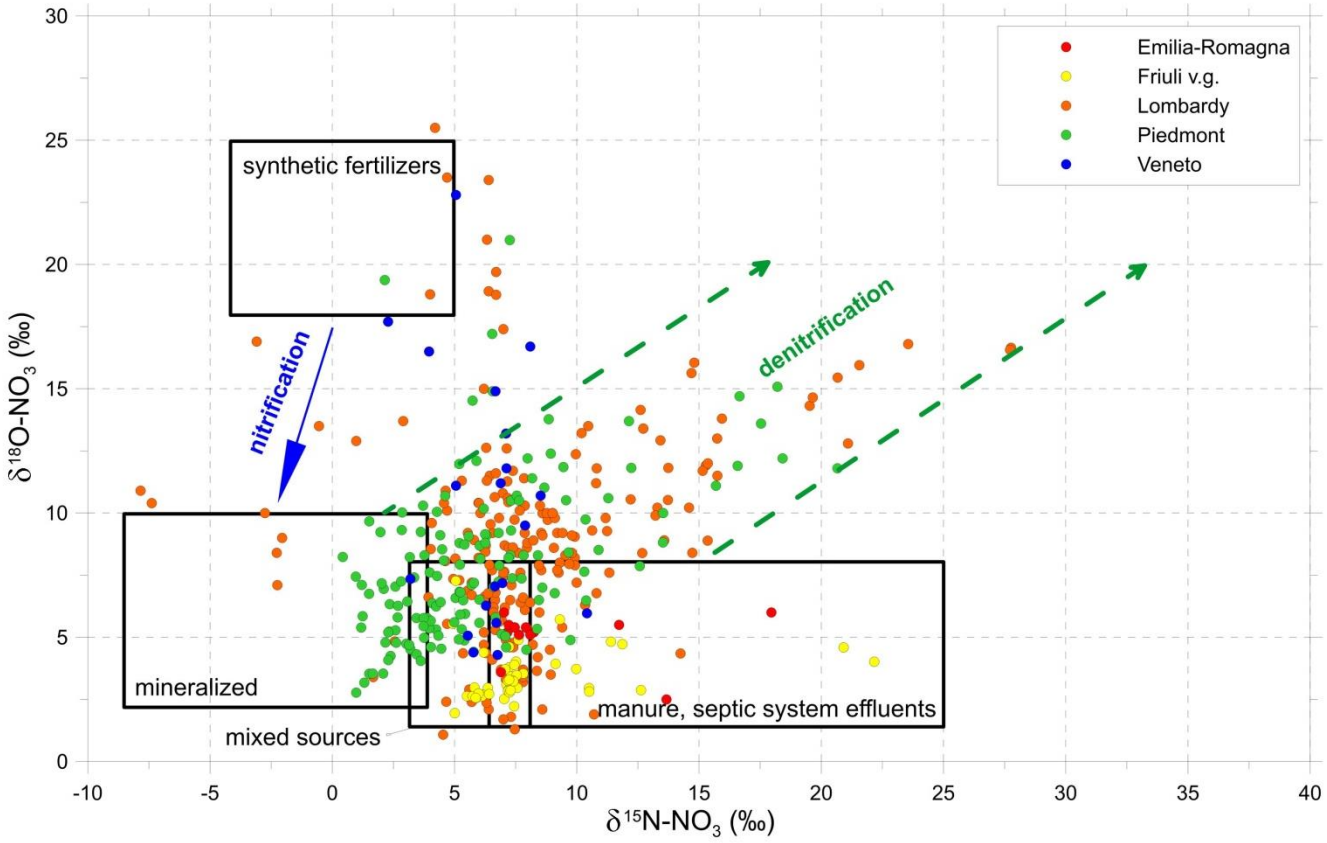


Fig. 11 - $\delta^{18}O_{NO3}$ vs $\delta^{15}N_{NO3}$ values in groundwater. Compositional fields and nitrification-denitrification trends from Sacchi et al. (2013), modified after Clark and Fritz (1997).

### *4.4 Insights provided by B isotopes*

Compared to the consolidated application of $\delta^{15}N$ to contamination studies, the associated use of $\delta^{11}B$ represents a promising but still subordinated tool, as testified by the very few data available

in the database of the studied area (both for B concentrations and isotopic compositions), compared to the large set of nitrate isotope data.

Currently, boron concentration values recorded in the database range between b.d.l. to 672 μg/l, and $\delta^{11}B$ values vary between -1.4 and +36.3‰ vs NBS-951 (n=27). A frequency histogram for the isotopic compositions (Fig. 12) shows the non-normal distribution of the data, with two populations characterized by different isotopic compositions, one around +10‰ and a second around +22‰. Comparing this distribution of $\delta^{11}B$ signatures to that recorded in Italian groundwaters (Pennisi et al., 2013), the value of +10‰ can be considered near to the mean geogenic value (+8.2 ‰) that characterizes the Italian alluvial aquifers. On the contrary, the higher $\delta^{11}B$ mode value (+22‰) clearly evidences inputs either of a sea water or of an animal manure component, both characterized by $^{11}B$-enriched signatures (Palmer and Swihart, 1996; Widory et al., 2005).

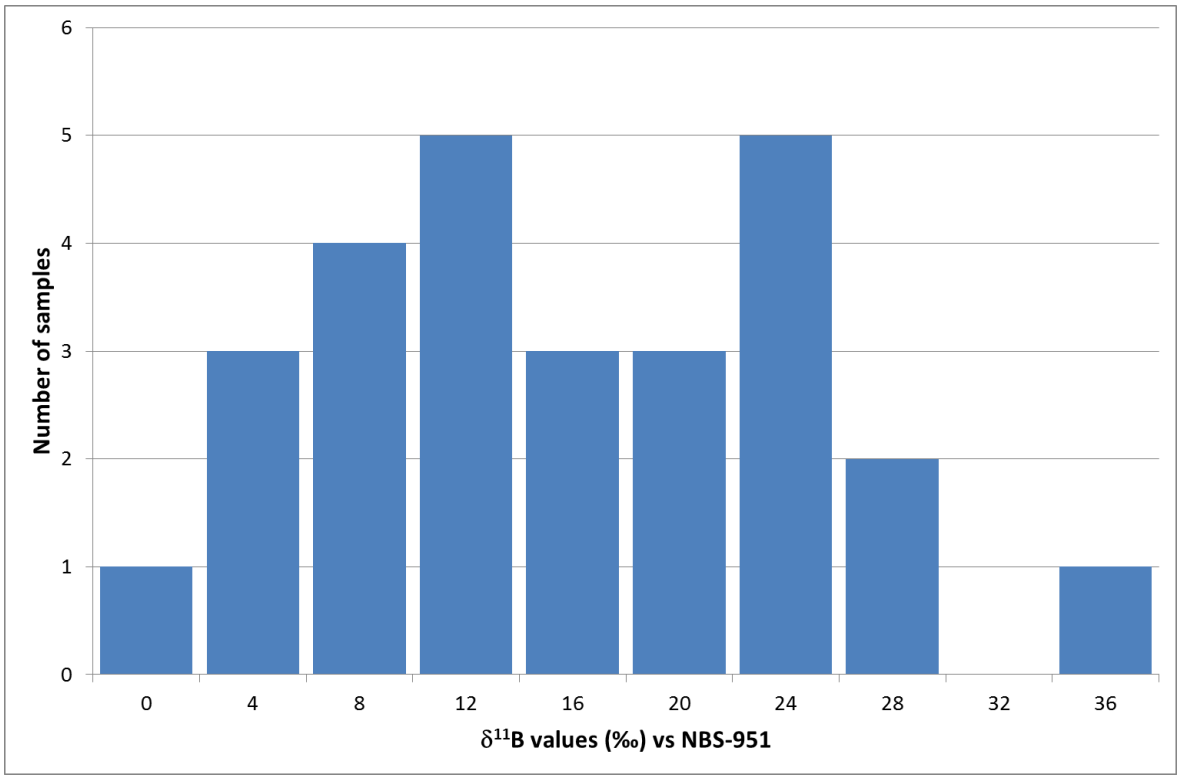


Fig. 12 – Frequency histogram of $\delta^{11}B$ values in groundwater. Values on the x-axis represent the interval's upper limit.

Together with the need to increase the number of values in the database, the application of the B systematics in the study area is challenged by the poor definition of the compositional end-members, both in terms of natural background and of potential sources of contamination. The application of the coupled $\delta^{15}N$ - $\delta^{11}B$ toolbox needs to identify the isotopic signature/s of the anthropogenic sources related to the given study site under investigation. As an example, boron in liquid animal manure reflects the boron signature of food and its fractionation eventually occurring from ingestion to the excretion pathway (i.e. urine). For piggery, a significant role in the pig manure signature can be played by the origin (marine *versus* non-marine) of the salt (NaCl with

554 1% boron) supplied with feeding. While concentrations and isotopic compositions of contaminants
555 are reported for given sites in France and the USA (see ISOBORDAT "Contaminants" database and
556 references therein), B isotope data on sewage, manure or fertilizer are at present lacking In Italy.

557 As an original contribution of this work we report new data on the main products used in the
558 agricultural sector in Emilia Romagna (Tab. 1). The values obtained for synthetic fertilizers, sewage
559 water and pig manure are within the ranges defined in the literature for these substances (Widory
560 et al., 2004, 2005; Tirez et al., 2010).

561

| Sample | Name | $\delta^{11}$B‰ vs NBS-951 | r.s.d (‰) |
|---|---|---|---|
| 1 | Boric acid | -13.5 | 0.4 |
| 2 | Colemanite | -12.8 | 0.4 |
| 3 | Colemanite 40 | -8.1 | 0.27 |
| 4 | Borax pentahydrate | -0.3 | 0.45 |
| 5 | Ulexite | -3.5 | 0.44 |
| 6 | Nitrophoska Blu Spezial | 0.3 | 0.56 |
| 7 | Sewage treatment plant (Sassuolo) | 8.2 | 0.56 |
| 8 | Pig manure | 13.9 | 0.5 |
| 9 | NaCl Italkali (B=1%) | 31.8 | 0.45 |

562

563 Tab. 1 – Isotopic composition of anthropogenic boron sources in the Emilia Romagna region.
564 Samples 1 to 5 are compounds utilized in the ceramics industry in the Reggio Emilia and Modena
565 provinces; sample 6 is an industrial fertilizer frequently used in the Po Valley; sample 7 is the
566 outflow of a sewage treatment plant located in Sassuolo (Modena province); sample 8 is the dry
567 residue of pig manure collected in the Reggio Emilia area; sample 9 is halite used in pig breeding.

568 In the highly impacted areas of the Alpine foothills of Lombardy, Sacchi et al. (2013) produced the
569 first coupled data on B and N in groundwaters with the aim of discriminating the contamination
570 from agriculture and contamination from civil origin. The authors selected samples where the
571 isotopic composition of dissolved nitrates fell in the field of contamination from mixed or
572 anthropogenic organic matter sources, or in the field of denitrification; two waste waters from
573 sewage treatment plants were also analysed, whereas the isotopic composition of the other
574 contaminant sources was taken from the literature. In Lombardy, boron concentrations ranged
575 from 20 to 540 μg/l (displayed as 1/B in Fig. 13) and $\delta^{11}$B values from -1.4‰ to +26.2‰. The
576 sample with the lowest B concentration had a $\delta^{11}$B of +14.6‰, and was assumed to be the
577 geogenic, "uncontaminated" end-member. With the increase of B concentrations, a group of
578 samples shifted towards both more depleted $\delta^{11}$B values, suggesting contamination from sewage

and/or fertilizers (Seiler et al., 2005; Widory et al., 2005). Conversely, in other samples, an increase in both the B concentration and isotopic composition was observed with respect to the geogenic end-member, attributed to a contribution of anthropogenic boron sourced from animal manure (Widory et al., 2004; 2005). An increase in the geogenic boron concentration controlled by increasing water-rock interaction, was also evidenced by the lack of any significant shift in the $\delta^{11}B$ signature of water respect to the un-polluted signature in some Po basin samples (Fig. 13). By comparison, samples from the Emilia Romagna and Veneto regions show a lower range of $\delta^{11}B$ but higher B concentrations, suggesting a higher contribution of either sewage or synthetic fertilizers.

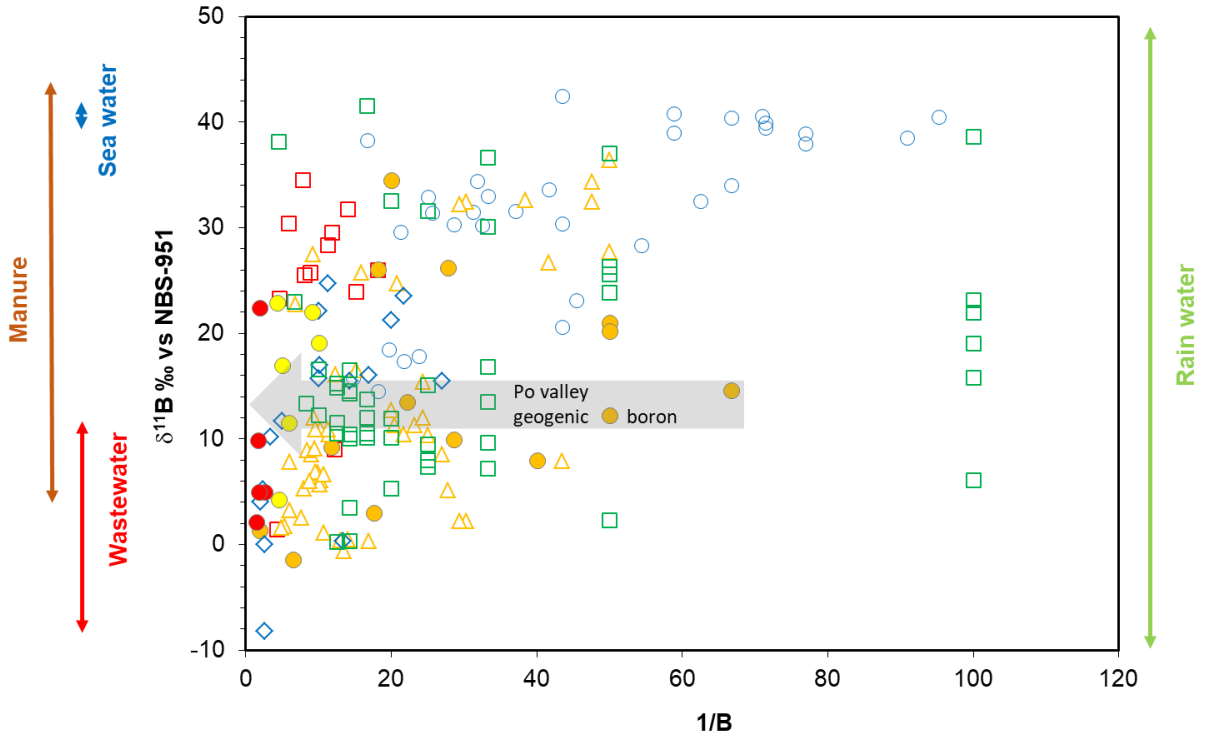


Fig. 13 - $\delta^{11}B$ vs 1/B plot of groundwater from Northern Italy (full dots: yellow = Friuli V.G.; orange = Lombardy; red = Emilia Romagna), and literature data from low geogenic-B environments (empty symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles = Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017). $\delta^{11}B$ compositional ranges of contaminants after Widory et al., 2004, 2005; Tirez et al., 2010; range for rainwater from the ISOBORDAT database (Pennisi et al., 2013). Boron concentration in mg/l.

In Fig 13, data from the investigated area are compared to literature data from studies where the $\delta^{15}N$ - $\delta^{11}B$ tool was applied in low geogenic-B environments. A large isotopic variation of almost 50‰ is associated to a boron concentration range of 10 – 1000 μg/l. Three end-members are distinguished, most of the samples resulting from a mixing between these sources. The high boron samples span over the whole range of $\delta^{11}B$, and mainly concentrate in the area were the "sewage" and "manure" isotopic signatures overlap. Fig. 13 also identifies a trend in literature data starting from low boron – high $\delta^{11}B$ composition (+40‰), indicating a boron enrichment in groundwater that occurs following the infiltration of meteoric water of marine origin. The decrease in $\delta^{11}B$ associated to the increase in B concentrations points to the two main anthropogenic boron

sources - animal manure and wastewater - recognized in the literature (Widory et al., 2004, 2005; Tirez et al., 2010). In this context, the newly defined isotopic signature of uncontaminated water from the Po alluvial aquifers ($\delta^{11}B$ = +13 ± 2.5‰) appears to be dominated by rainwater non-marine in origin or already modified during rock interaction.

Finally, Fig. 14 shows the $\delta^{11}B$ vs $\delta^{15}N_{NO3}$ plot of samples from the study area compared to other literature data obtained in groundwater from low geogenic-B environments. The compositional fields of the contaminants are represented as grey boxes (Widory et al., 2004, 2005; Tirez et al., 2010), and the red box evidences the compositional field defined for uncontaminated water from the Po alluvial aquifers. The plot confirms that both sewage and animal manure contribute to the nitrate pollution in the study area, as already indicated by Sacchi et al. (2013). Although isotopic data suggest that cattle manure is more concerned than pig manure as nitrate supplier to groundwater, this information partially contradicts the results obtained from animal husbandry data crossed with N isotopic data (see par. 4.2). Therefore, given the important implications for the agricultural sector, the unequivocal identification of the nitrate contamination sources in the study area still requires a better definition of the isotopic compositions of animal manure applied to agricultural fields, and the coupling of isotopic and farm census data .

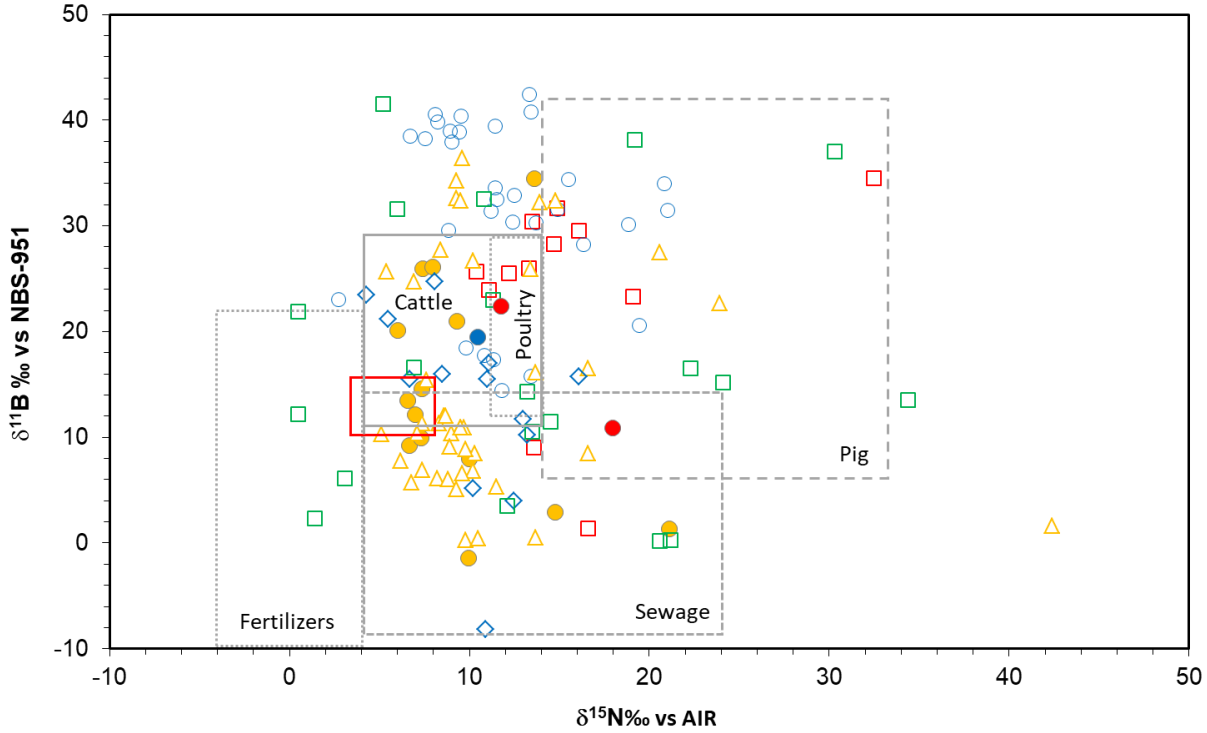


Fig. 14 - $\delta^{11}B$ vs $\delta^{15}N$ plot of groundwater from Northern Italy (full dots: orange = Lombardy; red = Emilia Romagna: blue = Veneto), and literature data from low geogenic-B environments (empty symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles = Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017). $\delta^{11}B$ and $\delta^{15}N$ compositional ranges: SF = synthetic fertilizers; Sew = sewage; CM = cattle manure; PM = pig manure (after Widory et al., 2004, 2005; Tirez et al., 2010). The red box corresponds to the compositional field defined for uncontaminated water from the Po alluvial aquifers.

## 5. Conclusions

In the last twenty years a remarkable number of nitrate isotopic data, often associated to oxygen, hydrogen and boron isotopic systematics have been produced in the Po plain area, mostly in local investigations. In this work, all the available nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and boron ($\delta^{11}B$) isotopic data, together with the hydrochemical composition, if available, were compiled in a comprehensive database, and some additional analyses were performed to fill the knowledge gaps in given areas or situations. Such an integration of data obtained in the groundwater hosted in a variety of sedimentary environments has allowed for their interpretation in a wider perspective, both providing an understanding of the N sources and dynamics in the shallow aquifers at the Po basin scale, and defining the more relevant processes governing nitrate contamination in Northern Italy. The conclusions of this work seek to assist regulators in devising sustainable management and remediation strategies.

In the investigated area, the most impacted groundwater is that hosted in the alluvial fans of the Alpine and Apennine foothills. This is due to a combination of high soil permeability and presence of intensive agricultural activities. Aquifers in these areas are characterized by fast circulation and by great depths of the water table. This finding indicates that, while the input of nitrates in these areas has led to present-day high concentrations, groundwater contamination would be quickly remediated if the N excess input were reduced. In addition, it is worth stressing that, in the study area, the general assumption that the deeper the water table, the higher the groundwater protection from contamination, is not verified. On the contrary, nitrate contamination is absent in most low plain areas, where the water table is shallow but soil permeability is lower. This is due to the presence of environmental conditions favourable to denitrification processes, as also indicated by other hydrochemical parameters (Fe, Mn, $NH_4^+$). While this is the general case in low plain areas, in certain cases (e.g. Poirino Plateau in Piedmont), denitrification, although present, is not sufficient to fully abate nitrates because of the high input coupled to the low dilution potential of the aquifer.

As the $\delta^{15}N$ median values are significantly correlated at the basin scale with pig farming, manure spreading represents one of the main nitrate sources in groundwater from agriculture, the other being synthetic fertilizers. Based on this evidence, pig manure management should be carefully re-evaluated and should be favoured in the low plain areas deprived of nitrates in groundwater, since the local hydrogeological setting allows nitrates to be metabolized in the environment with few consequences for the water resources.

Despite the relatively low number of available B isotope data, this systematics has provided interesting results in terms of nitrate contamination origin in such a low geogenic-B context. Indeed, it has proved the presence of another anthropogenic nitrate source, of civil origin, that is sewage in the study area. The garnering of all the data has allowed us to define the range of the expected geogenic B signature, and new results on the local B sources have been produced. This is a significant step forward for the use of the coupled $\delta^{15}N$ - $\delta^{11}B$ toolbox, as the application of the B systematics in the study area was previously limited by a poor definition of the compositional end-members, both in terms of natural background and of potential contamination sources. To further

enhance the application of this isotopic systematics, when sampling for nitrate isotopes, it would be advisable to collect and set aside a water aliquot (< 250 ml of untreated sample) that can be used for B isotope determinations even years later, should the investigation require it.

This georeferenced set of hydrochemical and isotopic data will lay the foundations for future monitoring activities and allow for an exploitation of already existing data from a different perspective, e.g. by advanced data treatment or modelling. Since the hydrogeological setting is similar throughout the Po and Veneto plains (Fig. 1 and Fig. 2), and shows common features to alluvial basins located near mountain ranges, the conceptual model of nitrate circulation and the processes affecting nitrate concentrations revealed by this study can be reasonably extrapolated to other areas of the watershed not yet investigated with isotopic tools, and serve as a reference for other study areas worldwide. In addition, based on the results of this study, different management options could be considered by decision-makers to reduce the impact of nutrients on water bodies. These relate to i) the amount of fertilizers used in agriculture, for example by tailoring their use to the actual crop needs. This option has already been adopted in municipalities declared as NVZ in order to obtain the derogation to the Nitrate Directive (European Commission, 2012); ii) the type of fertilizer used and the timing of application. This management option should balance the advantages and disadvantages of the use of manure and synthetic fertilizers in agricultural areas characterized by different soil permeabilities and agronomical practices; iii) the amount of water used for irrigation, in order to prevent the leaching of nutrients to the subsurface and increase their residence time in the soil; iv) the civil sources of N, for example by connecting isolated households to sewer pipes, checking the integrity of the sewage network and remediating leaching septic tanks.

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## References

ADAS, 2011. Economics report for NIT18 NVZ action programme impact assessment. 41. Available at
https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/82410/20111220nitrates-directive-consult-evid3.pdf

704 Agren, G. I., Bosatta, E., 1988. Nitrogen saturation of terrestrial ecosystems. Environ. Pollut. 54,
705 185-197

706 Appelo, C.A.J., Postma, D. 2005. Geochemistry, groundwater and pollution, 2nd edition. A.A.
707 Balkema Publishers, 649.

708 Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Bour, O., Molenat, J., Ruiz, L., de Montety, V., De
709 Ridder, J., Roques, C., Longuevergne L., 2012. Nitrate dynamics in agricultural catchments deduced
710 from groundwater dating and long-term nitrate monitoring in surface- and groundwaters. Sci.
711 Total Environ. 435, 167-178.

712 Aravena, R., Evans, M.L., Cherry, J.A., 1993.Stable isotopes of oxygen and nitrogen in source
713 identification of nitrate from septic tanks. Ground Water 31, 180-186.

714 Arduini, C., Dadomo, A., Martinelli, G., Porto, G., Sogni, R., Zelioli, A., 2007. Isotopic prospection in
715 high vulnerability area of the Milano province (Northern Italy). In: L. Ribeiro, A. Chambel, M.T.
716 Condesso de Melo (Eds), Proc. of the XXXV IAH Congress "Groundwater and ecosystems", Lisbon,
717 DOI: 10.13140/RG.2.1.4889.9289

718 Baily, A., Rock, L., Watson, C.J., Fenton O., 2011. Spatial and temporal variations in groundwater
719 nitrate at an intensive dairy farm in south-east Ireland: insights from stable isotope data. Agric.
720 Ecosyst. Environ. 144, 308-318.

721 Baker, L.A., Schussler, J., 2007. Whole watershed balances. Lakeline Magazine, Summer 2007, 17-
722 20.

723 Balderacchi, M, Perego, A., Lazzari, G., Muñoz-Carpena, R., Acutis, M., Laini, A., Giussani, A., Sanna,
724 M., Kane, D., Trevisan, M., 2016. Avoiding social traps in the ecosystem stewardship: The Italian
725 Fontanile lowland spring. Sci Total Environ 1, 539:526-35

726 Bartoli, M., Racchetti, E., Delconte, C.A., Sacchi, E., Soana, E., Laini, A., Longhi, D., Viaroli, P., 2012.
727 Nitrogen balance and fate in a heavily impacted watershed (Oglio River, Northern Italy): In quest
728 of the missing sources and sinks. Biogeosciences, 9 (1), 361-373.

729 Billen, G., Silvestre, M., Grizzetti, B., Leip, A., Garnier, J., Voss, M., Howarth, R., Bouraoui, F.,
730 Darracq, H., Lepisto, A., Kortelainen, P., Johnes, P., Curtis, C., Humborg,C ., Smedberg, E., Kaste,
731 O., Ganeshram, R., Beusen, A., Lancelot, C., 2011. Nitrogen flows from European regional
732 watersheds to coastal marine waters, in: Sutton, M.A., Howard, C.M., Erisman, J. W., Billen, G.,
733 Bleeker, A., Grennfelt, P.,van Grinsven, H., Grizzetti, B. (Eds.), The European Nitrogen Assessment.
734 Cambridge University Press, Cambridge, UK, pp. 271-297.

735 Boy-Roura, M. Nolan, BT., Menció, A., Mas-Pla, J., 2013. Regression model for aquifer vulnerability
736 assessment of nitrate pollution in the Osona region (NE Spain). J. Hydrol. 505, 150-162

737 Brancucci, G., 2001. Brief climatic framework of the Po Plain. In: G.B. Castiglioni and G.B.
738 Pellegrini (eds.), Illustrative Notes of the Geomorphological Map of Po Plain, Ch. 2, Geogr. Fis. Din.
739 Quat. Suppl. IV, 13-15.

740 Bronders, J., Tirez, K., Widory, D., Petelet-Giraud, E., 2012. Use of compound-specific nitrogen
741 ($\delta^{15}N$), oxygen ($\delta^{18}O$), and bulk boron ($\delta^{11}B$) isotope ratios to identify sources of nitrate-
742 contaminated waters: a guideline to identify polluters. Environ. Forensics 13, 32-38

743 Carraro, A., Fabbri, P., Giaretta, A., Peruzzo, L., Tateo, F., Tellini, F., 2013. Arsenic anomalies in
744 shallow Venetian Plain (Northeast Italy) groundwater. Environ. Earth Sci. 70, 3067-3084.

745 Castaldelli, G., Soana, E., Racchetti, E., Pierobon, E., Mastrocicco, M., Tesini, E., Fano, EA., Bartoli,
746 M., 2013. Nitrogen Budget in a Lowland Coastal Area Within the Po River Basin (Northern Italy):
747 Multiple Evidences of Equilibrium Between Sources and Internal Sinks. Environ. Manage. 52, 567-
748 580.

749 Cati, L., 1981. Idrografia e idrologia del Po. Ministero dei Lavori Pubblici, Servizio Idrografico.
750 Istituto Poligrafico e Zecca dello Stato, Roma, 310.

751 Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Raton.

752 Conti, A., Sacchi, E., Chiarle, M., Martinelli, G., Zuppi, G.M., 2000. Geochemistry of the formation
753 waters in the Po plain (Northern Italy): An overview. Appl. Geochem. 15, 51-65

754 Dadomo, A., Martinelli, G., 2005. Aspetti di idrologia isotopica in Emilia-Romagna. In: "Acqua e
755 copertura vegetale". Atti dei Convegni Lincei 216, 157-166, Roma

756 Debernardi, L., De Luca, D.A., Lasagna, M., 2008. Correlation between nitrate concentration in
757 groundwater and parameters affecting aquifer intrinsic vulnerability. Environ. Geol. 55, 539-558

758 De Luca, D.A., Dell'Orto, V., Destefanis, E., Forno, M.G., Lasagna, M., Masciocco, L., 2009. Assetto
759 idrogeologico dei fontanili della pianura torinese (Hydrogeological structure of the "fontanili" in
760 Turin plain). Rendiconti Online Società Geologica Italiana 6, pp. 199-200.

761 De Luca, D.A., Destefanis, E., Forno, M.G., Lasagna, M., Masciocco, L., 2014. The genesis and the
762 hydrogeological features of the Turin Po Plain fontanili, typical lowland springs in Northern Italy.
763 Bull Eng Geol Environ 73, 409-427

764 Edmunds, W.M., Shand, P.(Eds), 2008. Natural groundwater quality, Wiley-Blackwell, 488

765 Elmi, G., Sacchi, E., Zuppi, G.M., Cerasuolo, M., Allais, E., 2013. Isotopic estimation of the evapo-
766 transpiration flux in a plain agricultural region (Po plain, Northern Italy). Appl. Geochem. 34, 53-
767 64.

768 European Commission, 1991. Directive 91/676/EEC. Council Directive of 12 December 1991
769 concerning the protection of waters against pollution caused by nitrates from agricultural sources.
770 Off. J. Eur. Commun. L 375 , 1-8. Available at: http://eur-
771 lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1991:375:0001:0008:EN:PDF

772 European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the Council
773 of 23 October 2000 establishing a framework for Community action in the field of water policy,

774 Offic. J. Eur. Commun. L 327, 1-72. Available at: http://eur-
775 lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2000:327:0001:0072:EN:PDF

776 European Commission, 2011. Commission implementing decision of 3 November 2011 on granting
777 a derogation requested by Italy with regard to the Regions of Emilia Romagna, Lombardy,
778 Piedmont and Veneto pursuant to Council Directive 91/676/EEC concerning the protection of
779 waters against pollution caused by nitrates from agricultural sources (2011/721/EU). Offic. J. Eur.
780 Union L 287, 36-41. Available at: http://eur-
781 lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:287:0036:0041:EN:PDF

782 EEA European Environment Agency, 2005. Source Apportionment of Nitrogen and Phosphorus
783 Inputs into the Aquatic Environment. EEA Report 7, 48.
784 <http://www.eea.europa.eu/publications/eea_report_2005_7>.

785 Fratianni, S., Acquaotta, F., 2017. The climate of italy. In: M. Soldati and M. Marchetti (eds.),
786 Landscapes and Landforms of Italy, World Geomorphological Landscapes. Springer Springer
787 International Publishing AG, 29-38.

788 Fumagalli, N., Senes, G., Ferrario, P.S., Toccolini, A., 2017. A minimum indicator set for assessing
789 fontanili (lowland springs) of the Lombardy Region in Italy. European Countryside 9, 1-16

790 Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A.,
791 Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: Recent trends,
792 questions, and potential solutions. Science 320, 889-892.

793 Giambastiani, BMS ., Colombani, N., Mastrocicco, M., 2015. Detecting Small-Scale Variability of
794 Trace Elements in a Shallow Aquifer. Water Air Soil Pollut. 226, 7

795 Giuliano, G., 1995. Ground water in the Po basin: some problems relating to its use and protection.
796 Sci. Total Environ. , 171, 17-27.

797 Giuliano, G., Mari, G.M., Cavallin, A., De Amicis, M., 1998. Ricerca sulla vulnerabilità naturale e sul
798 rischio di inquinamento delle acque sotterranee nella pianura padana e veneto-friulana: carta
799 della infiltrabilità regionale, carta idrogeologica regionale, carta della vulnerabilità regionale
800 (scala1:500000). Memorie descrittive della Carta Geologica d'Italia 56, 1-102

801 Guffanti, S., Pilla, G., Sacchi, E., Ughini, S., 2010. Characterization of the quality and origin of
802 groundwater of Lodigiano (Northern Italy) with hydrochemical and isotopic instruments. Italian
803 Journal of Engineering Geology and Environment 1, 65-78

804 ISO4, 2005. Monitoraggio isotopico delle acque sotterranee in Provincia di Treviso, mediante
805 l'analisi degli isotopi stabili di ossigeno, idrogeno, carbonio e dei nitrati. Unpublished report,
806 Provincia di Treviso

807 ISTAT, 2010. 2010AgriculturalCensus. Available at http://dati-
808 censimentoagricoltura.istat.it/Index.aspx?lang=en&SubSessionId=e907b55d-8514-4899-880d-
809 cb62d6106cec&themetreeid=-200

Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen in ecosystems, in: Michener, R., Lajtha, K. (Eds), Stable isotopes in ecology and environmental science, Blackwell Publishing Inc., Oxford UK, 2nd edition, 375-449.

Komor, S.C., 1997. Boron content and isotopic composition of hog manure, selected fertilizer, and water in Minnesota. J. Environm. Qual. 26, 1212-1222.

Lasagna, M., De Luca, D. A., Debernardi, L., Clemente, P., 2013. Effect of the dilution process on the attenuation of contaminants in aquifers. Environ. Earth Sci. 70, 2767-2784.

Lasagna, M., Franchino, E., De Luca, D.A., 2015. Areal and vertical distribution of nitrate concentration in Piedmont plain aquifers (North-western Italy). In: G. Lollino et al. (eds.), Engineering Geology for Society and Territory – Volume 3, River Basins, Reservoir Sedimentation and Water Resources, 389-392. Springer International Publishing Switzerland.

Lasagna, M., De Luca, D.A., Franchino, E., 2016a. Nitrate contamination in the western Po Plain (Italy): the effects of groundwater and surface water interactions. Environ. Earth Sci. 75, 1-16.

Lasagna, M., De Luca, D.A., Franchino, E., 2016b.The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. Environ. Earth Sci. 75, 961

Lasagna, M., De Luca, D., Sacchi, E., Bonetto, S., 2006. Studio dell'origine dei nitrati nelle acque sotterranee piemontesi mediante gli isotopi dell'azoto. Giornale di Geologia Applicata 2, 137-143

Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. J. Hydrol. 270, 75-88.

Lorimor, J., Powers, W., Sutton, A., 2004. Manure characteristics. Manure Management Systems Series MWPS-18, Section 1, II Ed., available at: http://msue.anr.msu.edu/uploads/files/ManureCharacteristicsMWPS-18_1.pdf (last accessed May 2017)

Maffei, M., Vigliotti, L., Martinelli, G., 2005. Misure di suscettività magnetica e analisi degli isotopi stabili in carote della pianura padana datati tramite Cabonio 14. In Scialoja M.G.(Ed.), Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilizzazione. ARPA, Agenzia Regionale Prevenzione e Ambiente dell'Emilia-Romagna. I Quaderni di ARPA, Bologna, 181-196.

Mantovi, P., Fumagalli, L., Beretta, G.P., Guermandi, M., 2006. Nitrate leaching through the unsaturated zone following pig slurry applications. J. Hydrol. 316, 195–212

Martinelli, G., Chahoud, A., Dadomo, A., Fava, A., 2014a. Isotopic features of Emilia-Romagna region (North Italy) groundwaters: Environmental and climatological implications. J. Hydrol. 519, 1928-1938

844 Martinelli, G., Castagna, M., Pennisi, M., 2014b. Il monitoraggio del Boro nel sito contaminato
845 nazionale Sassuolo-Scandiano (Area del Distretto Ceramico di Modena e Reggio Emilia. In: Farina
846 M., Marcaccio M., Zavatti A.(Eds) Esperienze e prospettive nel monitoraggio delle acque
847 sotterranee: il contributo dell'Emilia-Romagna, 332-354, Pitagora Editrice, Bologna

848 Martinelli, G., Fava, A., Chahoud, A., Dadomo, A., 2014c. Il monitoraggio isotopico nelle acque
849 sotterranee in Emilia-Romagna. In: Farina M., Marcaccio M., Zavatti A.(Eds) Esperienze e
850 prospettive nel monitoraggio delle acque sotterranee: il contributo dell'Emilia-Romagna, 332-354,
851 Pitagora Editrice, Bologna

852 Martinelli, G., Dadomo, A., Italiano, F., Petrini, R., Slejko, F.F., 2016. Geochemical monitoring of the
853 2012 Po Valley seismic sequence: A review and update. Chem. Geol., in press
854 http://dx.doi.org/10.1016/j.chemgeo.2016.12.013.

855 Matiatos I., 2016. Nitrate source identification in groundwater of multiple land-use areas by
856 combining isotopes and multivariate statistical analysis: A case study of Asopos basin (Central
857 Greece). Sci. Total Environ. 541, 802-814.

858 McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal
859 aquifer systems. Ground Water 46, 259-271.

860 Menció, A., Mas-Pla, J., Otero, N., Regàs, O., Boy-Roura, M., Puig, R., Bach, J., Domènech, C.,
861 Zamorano, M., Brusi, D., Folch, A., 2016. Nitrate pollution of groundwater; all right…, but nothing
862 else? Sci. Total Environ. 539, 241–251

863 Minelli, A., Ruffo, S., Stoch, F., Cosentino, A., La Posta, A., Morandini, C., Muscio, G., Lapini, L.,
864 Paradisi, S., Sburlino, G., Solari, M., 2002. Risorgive e fontanili. In: Acque sorgenti di pianura
865 dell'Italia Settentrionale, Ministero dell'Ambiente, Museo Friulano di Storia Naturale, Comune di
866 Udine, 13-28

867 Ministry for Environment, Land and See, Ministry of Agriculture, Food and Forestry Policies,
868 regions of Piedmont, Lombardy, Veneto, Emilia-Romagna and Friuli Venezia Giulia, 2010. Request
869 from Italy for a derogation under paragraph 2(b) of Annex III to Directive 91/676/EEC from the
870 limit of 170 kilograms of Nitrogen per hectare per year from livestock manure. Available at:
871 http://www.regione.piemonte.it/ambiente/valutazioni_ambientali/dwd/nitrati/documento%20te
872 cnico%20scientifico%20CRPA.pdf (last accessed March 2017)

873 Nestler, A., Berglund, M., Accoe, F., Duta, S., Xue, D., Boeckx, P., Taylor, P., 2011. Isotopes for
874 improved management of nitrate pollution in aqueous resources: review of surface water field
875 studies. Environ. Sci. Pollut. Res. 18, 519-533.

876 Palmer, M.R., Swihart, G.H., 1996. Boron isotope geochemistry: an overview. Rev. Mineral. 33, 1-
877 862.

878 Panno, S.V., Hackley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the sources of nitrate
879 contamination in karst springs using isotopic and chemical indicators. Chem. Geol. 179, 113-128.

880 Pennisi, M., Adorni-Braccesi, A., Andreani, D., Gori, L., Sciuto, P.F., Gonfiantini, R., 2013. Isobordat:
881 an online database on boron isotopes. In: Isotopes in Hydrology, Marine Ecosystems and Climate
882 Change Studies. Proceedings from an International Symposium, Monaco, 2011, Vol.2, IAEA,
883 Vienna.

884 Petrini, R., Pennisi, M., Antisari, LV., Cidu, R., Vianello, G., Aviani, U., 2014. Geochemistry and
885 stable isotope composition of surface waters from the Ravenna plain (Italy): implications for the
886 management of water resources in agricultural lands. Environ. Earth Sci. 71, 5099-5111.

887 Pilla, G., Sacchi, E., Gerbert-Gaillard, L., Zuppi, G.M., Peloso, G.F., Ciancetti, G., 2005. Origine e
888 distribuzione dei nitrati in falda nella Pianura Padana occidentale (Province di Novara, Alessandria
889 e Pavia). Giornale di Geologia Applicata 2, 144-150

890 Pilla, G., Sacchi, E., Zuppi, G.M., Braga, G., Ciancetti, G., 2006. Hydrochemistry and isotope
891 geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a case
892 study from Lomellina, Po plain, South Western Lombardy, Italy. Hydrogeol. J. 14, 795-808.

893 Pilla, G., Sacchi, E., Ciancetti, G., 2007. Studio idrogeologico, idrochimico ed isotopico delle acque
894 sotterranee del settore di pianura dell'Oltrepò Pavese (pianura lombarda meridionale). Giornale di
895 Geologia Applicata, 59-74

896 Pilla, G., Torrese, P., Bersan M., 2010. Application of hydrochemical and preliminary geophysical
897 surveys within the study of the saltwater uprising occurring in the Oltrepò Pavese plain aquifer.
898 Boll. Geofis. Teor. Appl. 51, 301-323.

899 Provincia di Verona, 2001. Indagine idrogeologica, geochimica e geochimico-isotopica sugli
900 acquiferi della Lessinia. Rapporto Tecnico, Provincia di Verona-Settore Ecologia, Verona, 97

901 Puig, R., Soler, A., Widory, D., Mas-Pla, J., Domènech, C., Otero, N., 2017. Characterizing sources
902 and natural attenuation of nitrate contamination in the Baix Ter aquifer (NE Spain, using a multi-
903 isotope approach). Sci. Total Environ. 580, 518-532.

904 Risberg, K., Cederlund, H., Pell, M., Arthurson, V., Schnürer, A., 2017. Comparative characterization
905 of digestate versus pig slurry and cow manure – Chemical composition and effects on soil
906 microbial activity. Waste Manage. 61, 529–538

907 Rogora, M., Arisci, S., Marchetto, A., 2012. The role of nitrogen deposition in the recent nitrate
908 decline in lakes and rivers in Northern Italy. Sci. Total Environ., 417–418, 214-223.

909 Rotiroti, M., McArthur, J., Fumagalli, L., Stefani,a GA , Sacchi, E., Bonomi, T., 2017. Pollutant
910 sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy: Implications for drinking-
911 water supply. Sci. Total Environ. 578, 502-512.

912 Rotiroti, M., Sacchi, E., Fumagalli, L., Bonomi, T., 2014. Origin of Arsenic in Groundwater from the
913 Multilayer Aquifer in Cremona (Northern Italy). Environ. Sci. Technol. 48, 5395-5403.

914 Sacchi, E., Pilla, G., Allais E., Guallini, M., Zuppi, G.M., 2007. Tracing nitrification and denitrification
915 processes in a periodically flooded shallow sandy aquifer. Int. Symp. on Advances in Isotope
916 Hydrology and its role in Sustainable Water Resources Management, IAEA, Vienna 21-25 May
917 2007, IAEA-CN-151/33, vol. 2, 461-469

918 Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte, C.A., Laini, A., Pennisi, M., 2013. Origin and
919 fate of nitrates in groundwater from the central Po plain: Insights from isotopic investigations.
920 Appl. Geochem. 34, 164-180

921 Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Bottcher, M.E., Savarino, J., Escher, P.,
922 Eisenhauer, A., Erbland, J., 2013. Multi-isotope approach for the identification and
923 characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its
924 catchment area. Appl. Geochem. 34, 75-89

925 Seiler, R.L., 2005. Combined use of 15N and 18O of nitrate and 11B to evaluate nitrate
926 contamination in groundwater. Appl. Geochem. 20, 1626-1636.

927 Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Bolke, J.K., 2001. A bacterial
928 Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. Anal. Chem. 73,
929 4135-4153.

930 Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., Avanzino, R.J., 2000. A new
931 method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope
932 ratios. J. Hydrol. 228, 22–36.

933 Spruill, T. B., Showers, W. J., Howe, S.S., 2002. Application of classification-tree methods to
934 identify nitrate sources in ground water. J. Environ. Qual. 31, 1538-1549.

935 Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., Schindler, D., Schlesinger,
936 W.H., Simberloff, D. and Swackhamer, D., 2001. Forecasting agriculturally driven global
937 environmental change. Science 292, 281-284.

938 Tirez, K., Brusten, W., Widory, D., Petelet, E., Bregnot, A., Xue, D., Boeckx, P., Bronders, J., 2010.
939 Boron isotope ratio ($\delta^{11}$B) measurements in Water Framework Directive monitoring programs:
940 comparison between double focusing sector field ICP and thermal ionization mass spectrometry. J.
941 Anal. At. Spectrom. 25, 964–974.

942 Tonarini, S., Pennisi, M., Leeman W.P., 1997. Precise boron isotopic analysis of complex silicate
943 (rock) samples using alkali carbonate fusion and ion-exchange separation. Chem. Geol. 142, 129-
944 137.

945 Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger,
946 W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: sources and
947 consequences. Ecol. Appl. 7, 737-750.

948 Vitòria, L., Otero, N., Soler, A., Canals, A., 2004. Fertilizer characterization: isotopic data (N, S, O, C,
949 and Sr). Environ. Sci. Technol. 38, 3254-3262.

950 Vitòria, L., Soler, A., Canals, A., Otero, N., 2008. Environmental isotopes (N, S, C, O, D) to
951 determine natural attenuation processes in nitrate contaminated waters: example of Osona (NE
952 Spain). Appl. Geochem. 23, 3597-3611.

953 Vorlicek, P.A., Antonelli, R., Fabbri, P., Rausch, R., 2004. Quantitative hydrogeological studies of
954 the Treviso alluvial plain, NE Italy. Q J Eng Geol Hydrogeol 37, 1-7

955 Wendland, F., Berthold, G., Blum, A., Elsass, P., Fritsche , J.G., Kunkel, R., Wolter, R., 2008.
956 Derivation of natural background levels and threshold values for groundwater bodies in the Upper
957 Rhine Valley (France, Switzerland and Germany). Desalination 226, 160-168.

958 WHYMAP World-wide Hydrogeological Mapping and Assessment Programme, 2008. Groundwater
959 Resources Map of Europe. Available at:
960 https://www.whymap.org/whymap/EN/About/about_node_en.html (last accessed August 2017)

961 Widory, D., Kloppmann W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J., 2004. Nitrate in
962 groundwater: an isotopic multi-tracer approach. J. Contam. Hydrol. 72. 165-188

963 Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2013. Improving the
964 management of nitrate pollution in water by the use of isotope monitoring: the $\delta^{15}N$, $\delta^{18}O$, and
965 $\delta^{11}B$ triptych. Isot. Environ. Health Stud. 49, 1, 29-47.

966 Widory, D., Petelet-Giraud, E., Negrel, P., Ladouche, B., 2005. Tracking the sources of nitrates in
967 groundwater using coupled nitrogen and boron isotopes: a synthesis. Environ. Sci. Technol. 39,
968 539-548.

969 Xiao, J., Xiao, J.K., Jin, Z.D., He, M.Y., Liu, C.Q. (2013) Boron isotope variations and its geochemical
970 application in nature. Aust. J. Earth Sci. 60, 431–447.

971 Zini, L., Calligaris, C., Treu, F., Zavagno, E., Iervolino, D., Lippi, F., 2013. Groundwater sustainability
972 in the Friuli Plain. AQUA mundi Am07058, 041-054